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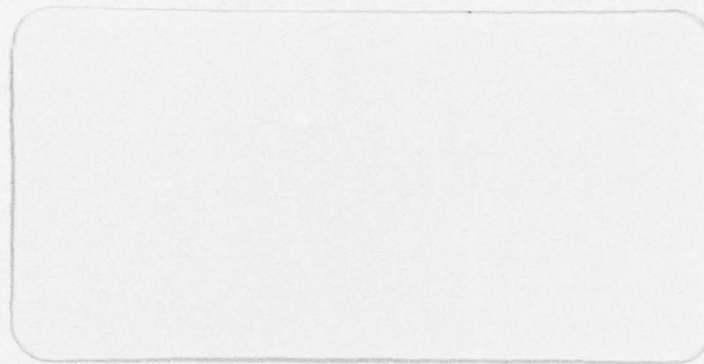
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DISSERTATIONS SYMPOSIUM ON CHEMICAL OCEANOGRAPHY

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SESSION I

ORGANIC MATERIAL AND PHYSICAL PROCESSES

ION ASSOCIATION AND ACTIVITY COEFFICIENTS IN ELECTROLYTE SOLUTIONS

Kenneth Stewart Johnson
Oregon State University

A model of aqueous electrolyte solutions was developed which allows the stoichio-metric association constant of an ion pair to be calculated in a mixture of two electrolytes that have one ion in common if the association constant of the other electrolyte is known and the activity of either electrolyte is measured. Measure-ments of the activity of HCl in aqueous mixtures with $HClO_4$ were used to calculate the stoichiometric association constant of HCl°. It was necessary to assume the association constant of $HClO_4^\circ$ was less than 10^{-2} in order to make this calcula-tion, that ion selective electrodes do not sense ion pairs, and that the free acti-vity coefficients of an electrolyte are a function only of the effective ionic strength. No other assumptions were made. The free activity coefficient is the activity coefficient obtained by dividing the activity by the free concentrations of the ions, rather than the total concentrations. The stoichiometric association constants are defined in terms of the free ion concentration also.

The results obtained for HCl° were then used to calculate the stoichiometric associ-ation constants of the alkali, alkaline earth, quaternary ammonium and manganese cations with chloride ion. These results were based upon measurements of the acti-vity of HCl in an aqueous mixture with the chloride salt of one of the cations men-tioned above. The stoichiometric association constants were fit to equations of the form:

$$\ln K^*_{MCl} = A + B\,I_e + C\,I_e^2$$

The effective ionic strength, I_e, is the ionic strength corrected for the effects of ion pair formation. The stoichiometric association constants of $NaSO_4^-$, KSO_4^- and $MgSO_4^\circ$ were each calculated from measurements of the activity of the correspond-ing chloride salt in a mixture with the sulfate salt of one of these cations. The stoichiometric association constant of $NaClO_4^\circ$ was obtained from measurements of the activity of NaCl in mixtures with $NaClO_4^\circ$.

The stoichiometric association constants of the ion pairs were used to calculate a chemical model for the distribution of species in mixtures of electrolytes, in-

cluding seawater. The speciation obtained in seawater is considerably different than previous estimates that ignored the formation of chloride ion pairs. The concentration of the chloride ion pairs with each cation is two to five times greater than the concentration of the corresponding sulfate ion pairs. Consequently, the free ion concentrations are much lower in this model than in previous ones.

The model was used to predict such properties of electrolyte mixtures as the activity of the solutes, the activity of water and the conductivity of electrolyte mixtures. Good agreement with experimental data was found in most cases. The root mean square error of total activity coefficients predicted in mixtures of two electrolytes was only two percent. Accurate and precise measurements of the total activity coefficient of NaCl in seawater were made to test the seawater speciation model. The agreement between the predicted and measured values in 35% seawater was better than one percent.

The relative changes in the speciation and equilibrium properties of the pore waters of marine sediments, compared to the overlying seawater, were calculated with the model. It was found that significant changes in the second apparent carbonic acid dissociation constant and stoichiometric solubility products may occur due to the compositional changes caused by diagenetic processes.

ACTIVITY EFFECTS IN SEAWATER AND OTHER SALINE MIXTURES

Donald Richard White, Jr.
University of Florida

The non-ideal, thermodynamic behavior of seawater and other aqueous saline media has been investigated utilizing a variety of experimental techniques, namely electromotive force measurements, the isopiestic method, and accurate determinations of pH.

The mean activity coefficient of HCl, $\gamma_\pm$, has been accurately determined by EMF measurements in mixtures of HCl and $MgCl_2$ as a function of temperature and ionic strength fraction of $MgCl_2$, y. This has been carried out at ionic strengths applicable to seawater and, as expected, $\gamma_\pm$ decreases with increasing y and ionic strength, I, according to Harned's Rule:

$$\log \gamma_\pm = \log \gamma_\pm^o - (\alpha y)I$$

where $\gamma_\pm^o$ is the mean activity coefficient of HCl in pure HCl solution at any particular ionic strength, and α is the Harned slope.

Since NaCl and $MgCl_2$ are the major components of seawater, an artificial seawater solution was considered where Na_2SO_4 and KCl are replaced by NaCl, and $CaCl_2$ is replaced by $MgCl_2$. An extension of Harned's Rule is then:

$$\log \gamma_\pm^{tr} = \log \gamma_\pm^o - (\alpha' y_A + \alpha y_B)I$$

where $y_A = 0.706$ and $y_B = 0.294$. The term α' is the Harned slope obtained from an independent study of HCl-NaCl mixtures, and $\gamma_\pm^{tr}$ is called the trace activity coefficient of HCl and corresponds to the $\gamma_\pm$ which would actually be measured in this two-component seawater with only a trace of HCl. Results obtained in this fashion for $\gamma_\pm^{tr}$ duplicate the values for the "trace" activity coefficient of HCl actually measured in complete synthetic seawater (excluding sulfate) with 0.01 m HCl. This implies that the decrease of $\gamma_\pm$ with increase in I is due to ionic interactions involving NaCl and $MgCl_2$, and that the effects of other salts are minor. With the aid of a computer, the data have been fitted to the equations of Pitzer for solutions of mixed electrolytes and the mixing parameters determined.

-8-

Isopiestic measurements have been carried out on mixtures of electrolytes having to do with seawater, $NaCl-Na_2CO_3$ and $NaCl-SrCl_2$, and osmotic coefficients determined over the ionic strength range 0.3 - 6 mol kg^{-1}. Data on the mixtures were fitted to the current theories of Pitzer and Scatchard for mixed electrolytes. It was found that the osmotic coefficients can be fitted with good accuracy based on data from the single electrolytes alone and the inclusion of up to 3 adjustable mixing parameters. Determination of these best-fit parameters allows calculation of activity coefficients for the individual solute species and provides insight into the behavior of more complex mixtures such as seawater.

The problems of single-ion activity and residual liquid junction potentials in pH measurement have been addressed in a study of pH in buffered synthetic seawater at varying salinities at 25°C. Changes in salinity appear to have a marked effect on the liquid-junction potential and, in turn, lead to error in pH measurement. The magnitude of these errors and the steps necessary to correct them are currently being investigated.

VOLATILE ORGANIC COMPOUNDS IN SEAWATER

Philip M. Gschwend
Woods Hole Oceanographic Institution

Vapor phase stripping and solid adsorbent trapping were applied to seawater and related samples to concentrate volatile organic compounds. The concentrates were subsequently analyzed by glass capillary gas chromatography and combined gas chromatography-mass spectrometry. The compound identities and the spatial and temporal distributions of their concentrations were used to determine some sources, transformations, and transport mechanisms of organic matter in the sea.

Volatile organic compounds were determined in seawater samples from the Sargasso Sea, the western equatorial Atlantic, and the upwelling region off Peru. Pentadecane was present in all three areas in surface samples at 10-40 ng/kg and decreased to 1-2 ng/kg in the deep water. A source related to the transformation of the algal fatty acid, hexadecanoic acid, by zooplankton is proposed since anthropogenic and direct phytoplankton sources are unlikely. C_2-alkylated benzenes were found in the upwelled water off Peru at about 4 ng/kg in the surface (5 and 20 m), 3 ng/kg below the thermocline (100 m), and 2 ng/kg or less in deeper water. A surface or atmospheric source is required to produce this distribution. C_6-C_{10} aldehydes were also found in seawater from off Peru. The direct correlation of their concentrations with chlorophyll <u>a</u> and with oxygen indicated that they are derived from chemical oxidation of algal metabolites, for example, unsaturated fatty acids. Total volatiles in the oligotrophic Sargasso Sea were about 10-30 ng/kg while the biologically productive upwelling region off Peru contained up to 100 ng/kg.

The temporal variations of volatile organic compound concentrations were investigated in coastal seawater from Vineyard Sound, Massachusetts. Pentadecane and heptadecane showed large summertime concentration increases which were ascribed to benthic algal sources. Laboratory incubations of benthic algal samples supported this conclusion. The saturated hydrocarbons, from C_{13}-C_{17}, and alkylated benzenes and naphthalenes were all abundant after an oil spill several miles from the sampling site. C_2- and C_3-benzenes were the most persistently abundant volatile compounds and their concentrations were observed to be 2-10 times higher than average immedi-

ately after summer weekends, peak periods of tourist and recreational activities on Cape Cod. Naphthalene and its homologues were more abundant in the winter than in the summer. C_6-C_{10} aldehydes were observed year-round, but showed a concentration maximum at the time of the late-winter phytoplankton bloom. C_{12}-C_{15} aldehydes were also found in abundance at that time. Oxidation of algal matter by zooplankton or photochemically produced oxidizing agents may produce the aldehydes, since laboratory cultures of phytoplankton did not produce these oxygenated volatiles. An alkene, structurally similar to the known benthic algal gamone, fucoserraten, was also found in Vineyard Sound seawater and in the upwelling region off Peru. Its appearance in Vineyard Sound samples coincided with the period of expected algal reproductive activity in February and March. Dimethyl polysulfides were found in coastal seawater. They may be produced within the water from precursors such as methyl mercaptan or other known polysulfide metabolites. Total volatile concentrations in Vineyard Sound seawater varied between 200 and 500 ng/kg for the period from January to June. Maximum concentrations occurred during the late-winter phytoplankton bloom and again in the spring from anthropogenic inputs of hydrocarbons.

The highest concentrations of C_2- and C_3-benzenes found in Vineyard Sound seawater coincided with motorboat use in the immediate vicinity of the sampling station. The average year-round isomer distribution most closely resembled distributions from gasoline and auto exhaust dissolved in seawater, consistent with an inboard or inboard/outboard motorboat source. Atmospheric and runoff delivery of C_2- and C_3-benzenes to Vineyard Sound seawater during the period from spring through fall was concluded to be of lesser importance. The atmosphere may serve as a buffer for seawater concentrations of the aromatic compounds, supporting low concentrations in the winter and limiting high concentrations in the summer.

THE INTERACTIONS BETWEEN COPPER AND ORGANIC MATTER IN COASTAL SEAWATER

Mary Jo Spencer
University of Miami

The objective of this research is to further the understanding of the interactions between copper ions and the organic components of coastal waters. Since copper ions are toxic to organisms especially phytoplankton, the presence of organic chelators is thought to be important for preventing the occurrence of toxic effects. This research has been focused in three areas. The first involves the measurement of the complexing capacity of local waters, i.e., Biscayne Bay. The second area of research concerns the comparison of various techniques for concentrating the organic fraction from seawater. The third area involves the establishment of the chemical nature of these organic chelators.

The complexing capacity of Biscayne Bay waters varies from 2.4×10^{-2} to 0.16 micromoles (1.5 to 10 ppb Cu equivalents). The values are highest inshore and at low tide.

Several different techniques have been tested for their ability to concentrate the chelating organics. The strong chelators are completely retained by a "500 molecular weight" ultrafiltration membrane. This technique is, however, extremely slow. Neither chloroform, butanol, XAD-2 nor acetylated polyamide resin extracts the metal-ligand complex at natural seawater pH. A C-18 silica gel bonded phase trap removed only a small portion of the metal complexes at natural pH. This fraction was of molecular weight greater than 5,000. Present results indicate that much but not all of the chelating organics are trapped on XAD-2 resin when the solution pH is adjusted to 2. Further studies are being carried out involving the use of the other extraction techniques at ph 2.

The third research area is the most significant of the three but is, however, the most challenging experimentally. The question to be answered is: what is the chemical nature of these chelators? Since very little is known concerning the chemical nature of the majority of the organic matter in seawater, one starts out with very little to go on. One thing is certain, however. For an organic ligand

to be an effective copper chelator in seawater it must chelate so strongly
with copper as compared to metals such as calcium and magnesium that the high con-
centrations of these latter metals do   not completely tip the scales in their
favor.

A novel method has been established to determine the effective capability of the
organics to chelate copper as a function of molecular weight. A sephadex G-25
column equilibrated with seawater which has been spiked with a small amount of
copper (5-10 ppb) is utilized. The organic concentrate is applied to the column
and the metal content and the UV absorbance of the eluent measured simultaneously.
The presence of a chelator is marked by a metal content higher than the baseline
concentration. The results from a sample of coastal water indicate that the com-
plexing ligands have a range of molecular weights, and that the distribution of
UV absorbance has a maximum which occurs at a higher molecular weight than does
the maximum in the distribution of the copper chelators. Thus, the chelating
capability of a fraction is not proportional to its UV absorbance.

Further experiments will be performed in order to determine the chemical nature
of the organic chelators. These experiments involve the treatment of the organic
extract with reagents that selectively block or destroy certain types of potential
chelating sites and the application of this treated sample to the column to look
for changes in the chelating capacity.

The combined findings from the studies in the three research areas will result in
a more complete view of the chemistry of copper in coastal waters. The results
obtained may be specific to this geographic area but the techniques and the method-
ology involved are of general utility. However, further work will be needed to
ex-waters from different water bodies in order to determine how generally applicable
the results from Biscayne Bay are to the world's oceans.

VERTICAL TRANSPORTATION OF ORGANIC MATERIALS IN OCEANIC ENVIRONMENTS

Eiichiro Tanoue
Nagoya University

The diffusion-advection model has been applied to interpret the vertical profile of dissolved oxygen in the deep waters from various oceanic areas by several workers (Munk 1966, Kroopnick 1974). They found a dissolved oxygen consumption rate in the deep waters with the range from 10 to 116 ml $O_2/l\cdot yr$, which is equivalent to 3-34 $gC/m^2\cdot yr$ of the decay rate of organic materials (Handa 1977). To confirm this figure of the values, the actual determination of vertical fluxes of organic materials has been tried by many workers. The Water Research Institute tried to determine the vertical fluxes of organic materials in the northern North Pacific Ocean off the Aleutian Islands arc with the the sediment-trap system submerged to 0.1-5.25 km depth (Tanoue and Handa 1979a, b). Fresh sediments trapped by the system also were analyzed for organic compounds with special attention to determining their chemical and/or biochemical nature.

Sediment-trap systems were moored in the northern North Pacific (47°51.1'N, 176° 20.6'E) on July 13-August 14, 1978 and fresh sediments collected from depths of 0.1, 1.1, 2.2, 4.4 and 5.25 km. Analyzing for organic compounds of the fresh sediments obtained, the following results were obtained.

1) The total flux of organic carbon to the deep water was measured and ranged from 2.7 to 8.5 $mgC/m^2\cdot day$ which can be converted to 1.0-3.1 $gC/m^2\cdot yr$. These values are almost comparable with the values predicted by the diffusion-advection model applied to the vertical profile of dissolved oxygen in the deep waters.

2) The concentration of organic carbon and nitrogen in the fresh sediments was determined and ranged from 3.2 to 6.9% and from 0.46 to 1.1% without significant vertical trends respectively. The values of the organic carbon and nitrogen were far less than the organic carbon and nitrogen contents of the particulate matter which were determined to range from 15 to 38% and from 1.5 to 4.1% respectively. These facts clearly indicate that the organic composition of fresh sediments is definitely different from that of particulate matter suspended in

waters from the surface to depth.

3) Rhamnose, fucose, ribose, arabinose, xylose, mannose, galactose and glucose were identified by GC and GC-MS upon acid-hydrolysis of both fresh sediment and particulate matter. Mannose was found to be the dominant monosaccharide in the hydrolysate of fresh sediment, while particulate matter gave glucose as the dominant monosaccharide upon acid-hydrolysis. Fractional extraction and partial acid hydrolyses of polysaccharides from fresh sediments and particulate matter indicated that mannose found in the fresh sediments was a component of glucuro-nomannan generally occurring in diatoms as cell-wall polysaccharide, while the glucose found in the particulate matter was derived from cellulosic materials. Such differences in monosaccharide and polysaccharide compositions between the fresh sediments and particulate matter suggest that a vertically active trans-portation system must be enrolled for the supply of organic matter to the deep waters. It is likely that the carrier of organic matter for such a system may be the zooplankton fecal pellet, but not the particulate matter suspended in waters.

4) Thirty components of fatty acids ranging from C_{12} to C_{28} were identified by GC and GC-MS as methyl esters in the fresh sediments and phytoplankton collected from the Bering Sea and northern North Pacific Ocean. The fatty-acid composition of fresh sediments was similar to that of phytoplankton. Unsaturated fatty acids of C_{16} and C_{18}, being biochemically most labile, were abundant in the fresh sedi-ment as observed in phytoplankton, while no unsaturated fatty acids were found in the particulate matter collected from less than 500 m depth. These facts indicate that the main source of fatty acids in the fresh sediment may not be the particulate matter suspended in waters, and vertical transport of fatty acids must be rapid because biochemically labile fatty acids were found abundantly in the fresh sediments. None of these facts conflicts with the facts observed in the carbohydrate analyses of the fresh sediments and particulate matter.

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AN INVESTIGATION OF VERTICAL MIXING RATES IN FJORDS
USING NATURALLY OCCURRING RADON-222 AND SALINITY AS TRACERS

William Massie Smethie, Jr.
Lamont-Doherty Geological Observatory

Vertical profiles of naturally occurring radon-222 were measured in the bottom
water of Dabob Bay, Hood Canal, and Port Susan in Washington State and Lake Nitinat,
Narrows Inlet, Queens Reach, and Princess Louisa Inlet in British Columbia. Radon
concentration generally increased exponentially with depth during stagnant periods.
Values of the vertical eddy diffusion coefficient, K_z, were estimated from the ex-
ponential profiles using two mathematical models. One model, which assumed that
the excess radon distribution was controlled only by vertical mixing and that there
was no horizontal input from the sides, gave an upper limit for the value of K_z.
The other model, which assumed that radon input from the sides was mixed rapidly
into the interior of the basin, gave a lower limit for the value of K_z. The ranges
of K_z values obtained, in cm^2/sec, are: 0.14 to 0.63 for Dabob Bay, 6.1 to 36 for
Hood Canal, 0.17 to 1.14 for Port Susan, 0.12 to 0.71 for Queens Reach, and 1.26
to 3.9 for Princess Louisa Inlet. It was shown mathematically that it was unlikely
that horizontal mixing was rapid enough to eliminate horizontal gradients of excess
radon and horizontal gradients were observed. Thus, it appears that the lower limit
for the value of K_z is unrealistically low. In Dabob Bay and Port Susan, the excess
radon concentration was uniform in the bottom 4 to 6 m indicating that there was a
zone of rapid vertical mixing adjacent to the sediment-water interface.

Excess radon in the upper water of Lake Nitinat, Princess Louisa Inlet, and Narrows
Inlet was high at the surface and decreased with depth. The source of the excess
radon was stream and river water flowing into the fjords. In Narrows Inlet values
of K_z were estimated from the excess radon profiles to be 0.23 to 0.47 cm^2/sec across
the fresh water-salt water interface in the upper 5 m and 0.9 to 3.1 cm^2/sec between
5 and 30 m depth.

The radon production rate of sediments collected from the fjords investigated in
this study ranged from $\sim$ 0.1 atoms/min/gm(dry) for Lake Nitinat (a permanently
anoxic fjord) to $\sim$ 2.1 atoms/min/gm(dry) for Dabob Bay, and this variation was re-

flected in the bottom water concentration of excess radon, which ranged from near 0 in Lake Nitinat to $\sim$ 450 dpm/100 liters in Dabob Bay. The reason for this variability is not known, but radon production rates were lowest for anoxic sediments.

The standing stock of excess radon was 2 to 8 times the molecular diffusive flux of radon across the sediment-water interface; this was apparently caused by a combination of horizontal diffusion of excess radon from the fjord sides and biological or physical stirring of the sediments, which enhances the release of radon from the sediments.

Values of K_z estimated from salinity decreases during stagnant periods for Narrows Inlet increased from $\sim$ 0.08 to $\sim$ 0.2 cm^2/sec between 44 and 72 m and Princess Louisa Inlet increased from 0.15 to 2.7 cm^2/sec between 60 and 150 m and then decreased to 0.54 cm^2/sec at 170 m.

Values of K_z for bottom water varied over two orders of magnitude among fjords investigated in this study and this variation was apparently caused by different inputs of tidal energy into vertical mixing in the different fjords. The value of K_z generally increased with depth in the deep water of fjords as stratification decreased and the presence of internal sills greatly enhanced the rate of vertical mixing. In Narrows Inlet there was a high energy regime in the surface water and a low energy regime in the deep water and K_z was inversely related to stratification in both regimes.

A vacuum gas extraction system was built to extract radon from water. The extraction time for a 23-liter sample is 15 minutes with a 98.5% recovery. Total processing time (extraction, purification, and transfer of radon to a counting cell) is 40 minutes per 23-liter sample.

SESSION II

SEDIMENTS

THE GEOCHEMISTRY OF RADIUM-226 AND RADIUM-228 IN MARINE DEPOSITS

James Kirk Cochran
Yale University

One of the earliest marine geochemical problems involving natural radionuclides arose from the discovery that ^{226}Ra (1622 y half-life) is enriched in deen-sea sediments and ferromanganese nodules relative to nearshore sediments and sedimentary rocks. The removal of radium to the deep ocean bottom was inferred to be responsible for this effect until it became evident that the abundance of ^{226}Ra in seawater far exceeds production from the very low concentration of its parent, ^{230}Th, or the supply from streams. Indeed, marine sediments are the primary source not only of ^{226}Ra but also ^{228}Ra (5.75 y half-life), derived from ^{232}Th decay. The uniqueness of this source, as well as the pronounced geographic and depth variations, make the radium isotopes potentially useful chronometers for oceanic mixing processes. The successful application of the radium tracer depends on adequate characterization of the mechanisms of its release from sediments. This study tries to understand how ^{226}Ra and ^{228}Ra are mobilized in nearshore and deep-sea sediments and how this relates to their observed oceanic distributions.

Based on a suite of cores collected from the Atlantic and Pacific oceans, the flux of ^{226}Ra from deep-sea sediments varies with geography and sediment type by at least a factor of 50. The extremes are represented by rapidly accumulating calcareous sediment from the Mid-Atlantic Ridge and slowly accumulating siliceous ooze-red clay of the north equatorial Pacific. A core from the Mid-Atlantic Ridge has a sediment accumulation rate of 2.9 cm/ky and is characterized by an 8 cm thick zone of active biological mixing in which long-lived nuclides like ^{14}C and ^{230}Th are homogenized. Calculation of the expected ^{226}Ra profile using a box model for the mixed layer indicates that radium is slightly depleted in this zone; but, deeper than 8 cm, the sediments behave like a closed system for ^{226}Ra.

In contrast, the slowly accumulating ($\sim$ 0.15 cm/ky) sediments of the north equatorial Pacific display the greatest deep-sea Ra fluxes observed in this study. In these cores, the interstitial water was separated from the sediment by a gas-operated piston squeezer and analyzed for ^{226}Ra and ^{228}Ra. Ra is enriched in the pore

water by a factor of 5 to 100 over that in near-bottom water, and the nature of the depth profiles permits application of a diagenetic model to describe Ra mobility in deep-sea sediments. Radium atoms are introduced to sediment-pore water by recoil processes associated with the decay of their thorium parents. Once in the pore water, Ra is subject to diffusion, adsorption, advection and radioactive decay. The ultimate escape of Ra to the overlying water is modified by the presence of traps in or on the sediment which decrease the flux of the diffusing nuclide. In the north equatorial Pacific, ferromanganese nodules forming at the sediment-water interface constitute such a trap. Although radium diffuses into the bottom sides of the nodules (in contact with the sediments), the high ^{230}Th concentration in the nodule top sides generates ^{226}Ra which diffuses out. A mass balance indicates that ferromanganese nodules represent a net sink for Ra.

Study of the pore water and sediment from cores collected in the muddy areas of Long Island Sound and Narragansett Bay shows that Ra is mobilized in estuarine sediments as well. The diagenetic model developed for Ra in deep-sea sediments can be applied to the nearshore. Two effects on the nearshore pore water Ra profiles not apparent in the deep sea are: (1) enhanced release of Ra in the upper few cm due to Mn recycling; and (2) the effects of irrigation and deep burrowing by the benthic fauna.

The fluxes of Ra determined from nearshore and deep-sea sediments are used to assess the oceanic Ra balance. A box model of the surface ocean indicates that the measured Ra fluxes from nearshore sediments can account for the surface Ra concentrations provided the average rate of supply of deep water to the mixed layer is about 20 cm/y, a value 10 to 20 times less than the deep water advection velocity. The variation in ^{226}Ra flux from deep-sea sediments is directly related to the amount of ^{230}Th present near the core top. The geographic variation in the ^{226}Ra flux follows the general increase in bottom water ^{226}Ra from Atlantic to Pacific. In particular, the high flux from the north equatorial Pacific sediments is reflected in the high ^{226}Ra concentrations found in deep waters of this region.

THE DISSOLUTION KINETICS OF BIOGENIC CALCIUM CARBONATE: LABORATORY MEASUREMENT AND GEOCHEMICAL IMPLICATIONS

Robin Scott Keir
Woods Hole Oceanographic Institution

The dissolution kinetics of calcite and aragonite in seawater are a very interesting phenomenon. They provide important clues to the physical-chemical mechanisms which control dissolution of these minerals, and along with oceanographic observations, they provide important evidence regarding the nature of the dissolution of these minerals in the deep sea.

In this study, a new method of measurement of particle-liquid heterogeneous kinetics was developed, and a new technique for solubility measurement employed. Dissolution rate as a function of degree of undersaturation was measured on individual species of coccoliths and foraminifera, on various sediment-size fractions, on a collection of large pteropods and on synthetic calcite and aragonite powder. Results of this study indicate that all biogenic and synthetic calcium carbonate dissolves according to the rate law:

$$R = k(1-\Omega)^n$$

where $\Omega \equiv [Ca^{++}] [CO_3^{--}]/K_{sp}'$ and K_{sp}' is the apparent solubility of calcite or aragonite in seawater. In the case of all calcite samples, $n_c = 4.5 \pm .6$, while for aragonite $n_a = 4.2 \pm 1$. The rate constant, k, varies widely between samples. For foraminiferal, sediment, and synthetic calcite, k appears to have a rough inverse correlation with grain size. However, the coccoliths, *E. huxleyi* and *C. neohelis*, cultured in the laboratory, appear not to follow this rule, with rate constants an order of magnitude lower than expected.

Rate as a function of percent dissolution in the case of deep-sea sediment reflects progressive dissolution of fine material in well-stirred experiments. This appears to be discordant with the observations that deep-sea sediment becomes progressively fine-grain with increasing dissolution and that some coccolith species are preferentially preserved compared with the most resistant forams.

Rate as a function of percent dissolution in the case of individual species of forams appears to reflect the statistical variation in the thickness of the shell

assemblage. It also appears that the rate of dissolution is roughly correlated to the number of identifiable individuals.

In order to investigate the nature of dissolution at the sediment-water interface, a model was constructed which takes into account dissolution kinetics, sedimentation, bioturbation, standing crop of carbonate particles, and molecular diffusion in the pore water. The model predicts well the observed percent calcium carbonate in surficial sediment versus water depth throughout most of the Atlantic and Pacific oceans.

The model predicted rate constant appears to be two orders of magnitude lower than that of whole sediment in suspension at 1 atm and 20°C. However, the model predicted rate constant is comparable to that measured for coarse grain foraminiferal assemblages and individual species of forams. Thus, the implication is that the fine-grain material in sediment is somehow preferentially protected.

SEDIMENTARY GEOCHEMISTRY OF HYDROCARBONS FROM
NARRAGANSETT BAY, RHODE ISLAND:
INCORPORATION, DISTRIBUTION AND FATE

Terry Lee Wade
Old Dominion University

Determining the impact of petroleum pollution in estuarine environments is essen-
tial because of its biological importance. The geochemical fate and biological
effects of chronic petroleum addition to the productive Narragansett Bay estuary
was investigated. The two main objectives of this research were to determine:
(1) the geochemical distribution of hydrocarbons for Bay sediments; and (2) the
mode of incorporation, distribution and fate of saturated hydrocarbons in the
Marine Ecosystems Research Laboratory (MERL) ecosystem sediments.

The concentration of hydrocarbons (saturated, aromatic, biogenic, and anthropo-
genic) and chlorinated hydrocarbons (chlordane, DDT, and PCB's) in mid-Narragan-
sett Bay was determined to provide additional information on their geochemical
distribution. Anthropogenic materials (chlordane, DDT, PCB's and anthropogenic
hydrocarbons) generally decrease with increasing depth in a core and reach back-
ground levels at depths consistent with the geochronology of this area of the
Bay and the chronology of inputs of these materials. Bioganic materials (organic
carbon and biogenic hydrocarbons) remained fairly constant with increased depth
in a core. Size fractionation of two-core sections showed more hydrocarbons
(biogenic and anthropogenic) associated with the smaller size fraction (<45 μm to
>0.3 μm) in the surface-core section, while the lower section had slightly higher
concentration for these hydrocarbons in the larger size fraction (>45 μm). These
results indicate that the input of biogenic materials to this sedimentary environ-
ment has remained fairly constant over the time period covered by this core, while
the input of anthropogenic materials has increased dramatically. It appears that
the increased input of anthropogenic organic materials, including hydrocarbons,
to this estuarine environment is reflected by increased concentration of these
materials in the upper layers of the sediments.

The second part of this investigation focused on the incorporation, distribution
and fate of No. 2 fuel oil saturated hydrocarbons in sediments from the MERL eco-

systems. Periodic additions of No. 2 fuel oil to the ecosystems simulated a chronic input. After the initial addition of oil, trace amounts were detected in the sediments within two weeks, but substantial accumulation was not seen until approximately 135 days after the initial chronic oil addition. The majority of the No. 2 fuel oil saturated hydrocarbons was found to be associated with suspended material in the water. Size fractionation of both suspended material and sediments indicated the No. 2 fuel oil saturated hydrocarbons associate to a larger extent with the smaller size fraction (<45 μm). Most of the No. 2 fuel oil saturated hydrocarbons is apparently carried to the sediments associated with smaller particles (<45 μm to >0.3 μm). Once they reach the sediments, these particles with their associated No. 2 fuel oil saturated hydrocarbons have been detected at depths of 3 to 4 cm below the surface. Although only 7 percent or less of the No. 2 fuel oil saturated hydrocarbons added to the ecosystems was found in the sediments, once incorporated in the sediment these materials are relatively stable. The No. 2 fuel oil saturated hydrocarbons were easily detectable 185 days after the last oil addition.

Studies on the bay cores indicate that the input of anthropogenic hydrocarbons has increased dramatically over the past 100 years, while the input of biogenic hydrocarbons and total organic carbon has remained relatively constant. Studies in the MERL tanks indicate that a fraction of the petroleum hydrocarbons from a chronic input would be transported to the sediments associated with smaller size particles. Once in the sediments these materials appear to be relatively stable. This same process is probably responsible for transport of hydrocarbon materials to Bay sediments.

EARLY DIAGENESIS OF TRACE METALS IN NEARSHORE LONG ISLAND SOUND SEDIMENTS

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Sedimentary pore waters were obtained seasonally from two nearshore areas in Long Island Sound, Branford Harbor, Connecticut and Mystic River Estuary, Connecticut. The pore waters were collected, separated from the sediments and analyzed utilizing inert atmospheric and ultra-clean laboratory techniques in order to minimize any artifacts due to improper sampling and contamination. The pore fluids and the sediments were analyzed for a variety of major and minor components as well as the trace metals: Fe, Mn, Zn, Cu, Pb, Cd and Ag.

Sediments from these two areas were anoxic and bacterially mediated sulfate reduction was the major biogeochemical process taking place. As this process proceeds, SO_4^{2-} is consumed, sedimentary organic matter is oxidized and HS^-, PO_4^{3-}, NH_4^+, titration alkalinity and dissolved organic carbon (DOC) is produced. Diagenetic models were utilized to predict: (1) the observed pore-water titration alkalinity; (2) the source of reactive phosphate to the pore waters; and (3) to quantify the rate of sulfate reduction and nutrient production.

Diagenetic reactions involving the decomposition of organic matter and the dissolution, mobilization and precipitation of trace metals are also occurring in these sediments. In general, the concentrations of Fe, Mn, Zn, Cu, Pb and Ag were higher in the pore waters than the overlying Long Island Sound water, with the highest concentrations observed in the top 8 cm of the sediment. Due to the lack of precision of the Cd data no real trend could be delineated.

Sediment trace-metal data from Branford Harbor and the Mystic River Estuary indicate that the concentrations of Zn, Cu, Pb, Cd and Ag also decrease with depth, suggesting increased anthropogenic input of these metals into the sediments in the past 50 years. At the Branford Harbor site, Fe and Mn remained relatively constant with depth in the sediments, while at the Mystic River location, these two metals actually increased with depth. This increase was mirrored by an increase in organic carbon. Leaching experiments performed on the Branford Harbor sediments suggested

that Fe, Cu, Pb, Cd and Ag are first precipitated by iron monosulfide minerals and later incorporated into pyrite (i.e., FeS_2). Zinc and manganese appear to be incorporated into other authigenic phases. These phases possibly include: (1) a carbonate phase; (2) a fulvic acid organic matter phase; and (3) a ZnS phase.

Thermodynamic calculations indicate that metal-polysulfide and biosulfide complexes control the concentrations of dissolved Zn, Cu, Pb and Ag in these pore waters, while the concentrations of Fe, Mn and Cd are controlled by other inorganic species.

There is little evidence to suggest that trace metal-dissolved organic matter complexation plays a major role in controlling the solubility of these trace metals in the anoxic waters under investigation.

RATES OF SEDIMENT ACCUMULATION AND THEIR BEARING ON METALLOGENESIS ON THE NAZCA PLATE, SOUTHEAST PACIFIC

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More than 50 sediment cores from the Nazca plate have now been analyzed for sedimentation rates and bulk chemical composition. Sedimentation rates determined by direct assessment of unsupported ionium (^{230}Th) and microfossil zonation have been augmented by gamma-ray spectrometry techniques. The scanning gamma-ray spectrometer developed for this study possesses the advantages of rapid and non-destructive analysis, but the method was found to be susceptible to ^{222}Rn and ^{226}Ra disequilibrium effects. ^{226}Ra disequilibria apparently does not have an important effect on sedimentation rate determinations for sediments accumulating at rates of a few cm/10^3 years or greater, or for sediments possessing uniformly high adsorption capacities; a ^{226}Ra diffusion coefficient of 10^{-9} cm^2/sec or smaller was calculated for an East Pacific Rise (EPR) core, and is in agreement with previous work. ^{222}Rn disequilibria affects the determination of the absolute ^{230}Th (^{226}Ra) activity; up to about 80% of the ^{222}Rn can migrate, but this does not affect the sedimentation rate if the cores are scanned as an open system. A comparison of sedimentation rates determined by both direct (alpha) and indirect (gamma) ^{230}Th spectrometric techniques on six cores shows a general agreement between the two methods.

Regional patterns of metal accumulation were calculated from the sedimentation rates, using measured and calculated dry bulk densities and bulk chemical composition. The regional pattern of Fe accumulation parallels those for Mn and U, whereas those of Cu, biogenic Si, Al, Ti and Th generally display an inverse relationship. Multivariate factor analysis was employed to include correlation of accumulation rates for Na, K, Mg, Ca, Ba, Ni, Zn and P, and to distinguish hydrothermal from detrital, hydrogenous, biogenous and diagenetic associations. A ^{230}Th inventory, defined as the ratio of the ^{230}Th accumulation rate to the ^{230}Th seawater production rate, was employed as an index of sediment loss or enhanced sediment accumulation. The ^{230}Th inventory is greatest on the EPR, suggesting that some sediment ponding occurs there, and is generally lowest in the Bauer Basin, suggesting that sediment has been lost there by either coring disturbance, CaCO$_3$ dissolution or bottom current winnowing.

The regional pattern of Fe and Mn accumulation indicates that their rates of accumulation on the crest of the EPR vary by more than an order of magnitude; values near the equator (6°S) correspond to normal authigenic accumulation and exponentially increase toward 20°S latitude. The lower Fe and Mn accumulation rates in the norther EPR area suggest that either: (1) there is preferential loss of the metalliferous component to the north due to increased bottom current activity; (2) hydrothermal circulation is more intense to the south because of a lack of regional sediment cover or more extensive crustal fracturing; or (3) mantle heterogeneity exists along the rise crest. Bottom current winnowing is the most consistant explanation with the existing data on the distribution of conductive heat flow and crustal production along the EPR, and can explain both the variation in metal accumulation along the EPR crest and the appearance of a second area of metal enrichment in the Bauer Basin. Global budget calculations indicate that roughly 50% or more of the Mn produced at ridge crest may be lost to the adjacent seafloor by this mechanism, which has implications for the magnitude of hydrothermal input to the ocean and the origin of manganese nodules.

DISCRETE SUSPENDED PARTICLES OF BARITE AND THE BARIUM CYCLE IN THE OPEN OCEAN

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Several facts stress the necessity of more detailed knowledge of the barium cycle in the ocean. Indeed, although estimations of the overall cycle of barium in the ocean exist, very little information is available on the intermediary stages of the pathway. The generally accepted gross pathway is: incorporation of dissolved Ba by organisms in the SiO_2, $CaCO_3$ and organic matter fraction; partial redissolution of these biogenic materials at depth; release of Ba; and sedimentation of the residual fraction. Further, discussion exists in the literature concerning the exact source of the Ba that is accumulating in the sediments: settling of Ba enriched biogenic matter as opposed to hydrothermal processes.

Some of these problems have been studied during thesis' research by analyzing the role of the suspended-matter phase, which, up to recently, has not been intensively investigated. Some data, however, were available before starting the research. From measurements of Ba and Al in suspended matter it was deduced that more than 90% of the particulate Ba can be concentrated in phases other than aluminosilicates (i.e., continental material). (Darcourt 1973). Preliminary investigations at the University's laboratory, of suspended-matter samples with a scanning slectron microscope and electron microprobe (SEM-EMP equipment) revealed the presence of discrete barium- and sulphur-rich particles. (Jedwab 1974).

Suspended-matter samples, collected with 30 liter Niskin bottles during GEOSECS and other cruises in the Atlantic and Pacific oceans have been analyzed by SEM-EMP (allowing the study of individual micron-sized particles) and by neutron-activation analysis (INAA) for global, quantitative data on element concentrations. The geometric mean of all the INAA measurements of particulate Ba was 20 ng/kg seawater. The SEM-EMP investigations revealed the ubiquity of Ba- and S-rich particles in suspension throughout the water column. These particles had a mean diameter of 1 μm and were identified as barite crystals. They contain minor amounts of K and Sr. In surface water they occur together with discrete $SrSO_4$ particles which can contain various amounts of Ba. This suggests the existence, in surface water, of a solid

solution series with $BaSO_4$ and $SrSO_4$ as end members.

Barite, particle-size, volume analysis with the SEM and INAA measurement of total particulate Ba upon the same suspended matter samples revealed that, for intermediate and deep water, barite is the most important carrier of Ba in suspension, with up to 90% and more of total particulate Ba carried by this mineral. Other carriers are $CaCO_3$ and SiO_2 skeletons, particulate organic matter and aluminosilicates. Their contribution appears to be important in surface water, with 50% of total particulate Ba carried by biogenic components, and in bottom water, with 20% carried by aluminosilicates.

The origin of suspended barite is clearly biological. This is emphasized by the positive relationship between productivity and the total particulate barium content in the first 1000 m of the water column and by the occurrence in surface water of $(Ba, Sr)SO_4$ solid solutions of variable composition. Further, barite crystals were observed inside small organic pellets which may represent decaying organic matter. These observations suggest two possible processes of barite formation. Direct secretion of barite granules by organisms is known to occur in the benthic *Xenophyophorida* (*Rhizopoda*) (Tendal 1972). *Collosphaerid* and acantharid *Radiolaria* are known to secrete $SrSO_4$ crystals and it can be assumed that these organisms produce as well $(Sr,Ba)SO_4$ solid solutions and $BaSO_4$ crystals. Another possible process is the precipitation of barite inside sulphate-rich organic micro-environments, such as fecal material.

Suspended barite dissolves in a water column which is known to be undersaturated with respect to $BaSO_4$ (Church 1972). Application of a Stokes settling and dissolution rate model to the barite size distribution data resulted in a barite dissolution rate constant in sea water, and in a dissolution rate, J_{Ba}, of barite in the water column. The latter value ($0.4 \ \mu g.cm^{-2}.yr^{-1}$) is as large as the J_{Ba} term, deduced from estimated dissolution rates of SiO_2 and $CaCO_3$ tests ($0.5 \ \mu g.cm^{-2}. yr^{-1}$). The total J_{Ba} ($0.9 \ \mu g.cm^{-2}. yr^{-1}$) is important when compared with the mean river input of dissolved barium ($0.6 \ \mu g.cm^{-2}.yr^{-1}$) (Chan 1976) and emphasizes the important recycling of Ba in the water column. Further, the estimated production of particulate Ba ($1.35 \ \mu g.cm^{-2}. yr^{-1}$)—i.e., incorporation of Ba in SiO_2 and $CaCO_3$ skeletons and production of barite, the latter value deduced by considering barite to be pro-

duced during decomposition of organic matter in the surface waters—equilibrates the input of dissolved Ba ($1.5 \ \mu g.cm^{-2}. \ yr^{-1}$). The residual flux of suspended barite and of the estimated flux of Ba associated with fecal material towards the sediments is sufficient to account for known accumulation rates of Ba (0.5 to 1 0 $\mu g.cm^{-2}. \ yr^{-1}$ in the Atlantic) (Turekian 1966, 1968), with barite contributing for a maximum of $0.4 \ \mu g.cm^{-2}. \ yr^{-1}$.

To conclude, the thesis work has shown that barite crystals occur in suspended matter in the world's ocean. This barite is formed by biological activity and con-stitutes the main carrier of barium in suspended matter. The dissolution of this barite at depth is as important as the dissolution of other biogenic components of suspended matter carrying only trace amounts of Ba, but, which are present in large amounts. Part of the suspended barite can survive dissolution and can constitute an important fraction of the Ba that is accumulating in the sediments.

Note: This work was performed at the Université Libre de Bruxelles , Brussels, Belgium, under the direction of Professor J. Jedwab at the Laboratoire de Géochimie , and at the Centre des Faibles Radioactivités (CEA-CNRS) at Gif-sur-Yvette, France, under the direction of Professor R. Chesselet.

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TRACE METAL-ORGANIC MATTER INTERACTIONS IN ANOXIC MARINE SEDIMENTS DURING EARLY DIAGENESIS

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The transport processes and ultimate fate of many trace metals in anoxic marine sediments are very poorly understood. Several authors have invoked metal complexes with dissolved organic matter (OM) to explain enhanced solubilities observed for certain metal ions. However, the role that OM plays in solubilizing metals in marine pore waters has not been established because of inadequate characterization of dissolved "humic substances."

A persistent criticism of previous OM studies has been the use of chemically harsh extractants which degrade the OM. Relatively unaltered OM has been extracted with a method developed here that obviates the need for harsh treatments. Boxcores of anoxic marine sediments were collected in Great Bay, New Hampshire, and the dissolved OM was obtained by slurrying these sediments with artifical seawater. The clays and salts were removed from the slurry by centrifugation and ultrafiltration. The freeze-dried extract was analyzed for elemental composition and optical properties. All processing and storage of the anoxic sediment extract (ASE) employed a nitrogen atmosphere.

The molecular polarity and size of ASE was characterized by reversed-phase liquid chromatography (LC) and gel permeation chromatography, respectively. ASE can be described as a mixture of several components of relatively low polarity (comparable to 1,3 dihydroxybenzene or 1-pentanol) having a molecular weight of 60,000-80,000 daltons. The influences on the ASE structure of atmospheric oxygen, bacterial growth, NaOH, $Na_2P_2O_7$, and HCl have been assessed. In every instance, ASE is degraded to highly polar molecules of reduced molecular size, suggesting cleavage of the molecule with concurrent formation of oxygen-bearing functional groups. This indicates that utmost caution in sample handling is mandatory to avoid artifacts and that earlier studies by other workers, particularly metal-binding capacity measurements, may be misleading.

To study trace metal-ASE interactions, several existing techniques, previously not applied to anoxic marine samples, were adapted. A model system of well-characterized soil fulvic-acid (SFA) fractions was employed to assess suitability of these techniques.

Of interest was the identification and quantification of structural and metal chelation capacity changes as pH and ionic strength fluctuate. The SFA was separated by molecular weight into two fractions using gel filtration chromatography (GFC). The larger molecular weight fraction, SFA I, appears to increase its partial molar volume as pH increases. The data suggest that this is due to conformational changes upon rupture of hydrogen bonds when deprotonation of functional groups occurs. The size of the smaller molecular weight fraction, SFA II, remains unchanged. Analyses of the stoichiometries and stability constants of vanadyl ion complexes of the two SFA fractions were done by electron paramagnetic resonance spectroscopy (EPR) titrations of 2.5×10^{-3}M SFA solutions with vanadium at pH 5.0 and $\mu = 0.04$ M. A plot of the Scatchard equation gave the stoichiometries and stability constants for the various complexes.

The rotational correlation times of each VO^{2+}-SFA fraction, τ_R, were calculated from the linewidths of the EPR spectra and were used to estimate the molecular weight. The approximate molecular weights for the vanadyl ion complexes of SFA fractions I and II were 3800 and 350 daltons, respectively, and compared favorably with the values of 4100 and 335 daltons obtained independently from GFC studies.

The EPR and GFC data indicate that the vanadyl ion induces aggregation of SFA I producing a dimer "$(VO)_2(SFA\ I)_6$" according to the reactions:

$$2\ VO^{2+} + 6\ SFA\ I \qquad\qquad "(VO)_2(SFA\ I)_6" \qquad K_1 = 4.4 \times 10^5$$

$$6\ VO^{2+} + "(VO)_2(SFA\ I)_6" \qquad "(VO)_2(SFA\ I)_6(VO)_6" \qquad K_2 = 7.3 \times 10^3$$
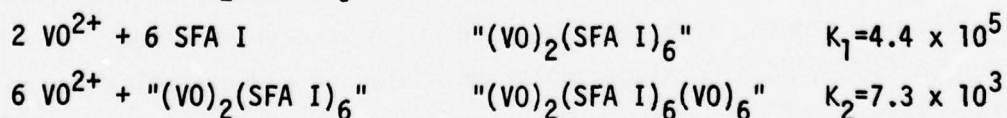
However, SFA II forms only a 1:1 complex with VO^{2+} that is remarkably similar to the weaker binding site of SFA I as the stability constant for SFA II is 1.0×10^4. The EPR spectra of the VO^{2+} complexes of both fractions have been modeled identically using bis(phthalato)(salicylato)oxovanadium(IV) and mono(salicylato)-oxovanadium(IV) complexes for SFA I and II, respectively.

These data demonstrate that the chelation capacity of each SFA fraction is different. This phenomenon appears to extend to ASE. Preliminary studies using LC to separate the ASE fractions, coupled to an atomic absorption spectrophotometer to measure metal concentrations, suggest that specific fractions bind Cu^{2+} and Cr^{3+} and do not bind Zn^{2+}, Cd^{2+}, and Hg^{2+}. Isolation of specific metal-binding fractions by LC is in progress. Future structural studies with nuclear magnetic resonance spectroscopy and metal-binding investigations by EPR are planned for these isolation products.

The above studies are designed to evaluate the importance of trace metal-OM interactions in early diagenesis. Results obtained to date have demonstrated the feasibility of using physico-chemical and separation techniques to characterize metal complexes of marine OM. These new approaches promise to provide information about natural processes which are only poorly understood at present.

FACTORS INFLUENCING THE PHASE PARTITIONING OF IRON AND ASSOCIATED ELEMENTS DURING EARLY DIAGENESIS IN SHALLOW MARINE SEDIMENTS

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Knowledge of diagenetic processes is essential for understanding the chemistry of sediments and their role in the overall geochemical balance of the oceans. It is also required for interpreting sedimentary rock records of ocean history. Continental shelves are important areas of diagenesis because of the high input of material from continental weathering. Therefore, in this dissertation, the phase partitioning and diagenesis of Fe and associated elements are examined in low-carbonate sediments from the outer Texas shelf of the Gulf of Mexico. A chemical approach is used, based on a sequential extraction scheme designed to remove successively more resistant forms of Fe, Mn, Zn, Cu, and Cr in sediment samples. Sulfate and solid S measurements are used to determine organic decomposition rates and the factors which influence these rates. Major cations and phosphate are also measured to determine their relation to Fe.

The results indicate that benthic organisms significantly affect the chemical environment of the shelf sediments, increasing the effective diffusion coefficient for sulfate by as much as an order of magnitude over non-bioturbated sediments. In addition, subsurface oxidation maxima are formed by the pumping activity of vertically-oriented tube-dwellers. Modelling of dissolved sulfate and solid-phase S (mainly pyrite) above and below the top oxidation maximum indicates that organic matter decomposition in the upper zone is at least three orders of magnitude more rapid than below that subsurface maximum. Less variation occurs between deeper zones of each core.

An investigation of P partitioning reveals that the forms of solid P vary greatly with depth. In reducing zones, a highly-reactive (1M HOAc-soluble) Mg-Fe-P clay association becomes the dominant form of P. Organic C/P ratios increase both with distance from shore and with depth in the sediment column, indicating preferential breakdown of P, similar to findings of other researchers.

Use of a 1M HOAc extraction enables measurement of exchangeable Fe, as well as Mg, K, and Ca. Ratios of dissolved to exchangeable Mg, K, and Fe indicate preferential uptake of Fe and K by the clays. In addition, partial correlation analyses suggest that some sort of control is exerted by non-pyrite reduced Fe (probably ferrous hydroxide) on the choice of major cation selected by the clay. This could be analogous to the formation of glauconite in the sulfide-poor reducing microenvironments of fecal pellets.

The calculated mass fluxes of Fe (0.2-8. μmoles Fe/cm^2/yr), Mn (0.08-1.7 μmoles Mn/cm^2/yr), and P (0.03-2. μmoles P/cm^2/yr) are intermediate in magnitude between flux values reported for anoxic sediments and estimated averages for the total ocean floor. Assuming these values are representative of the world's continental shelves, extrapolations suggest that the mass flux of these elements from shelf sediments is equal to or greater than the supply from the world's rivers, indicating the importance of the shelf environment in ocean geochemical balances.

A vertical box model, consisting of homogeneous redox layers within which reaction rates are constant, can be used to describe Fe diagenesis. The quantitative agreement between the model and observed Fe distributions is excellent in areas where benthic organisms are sparse. As horizontal gradients increase as a result of benthic activity, the one-dimensional model becomes more qualitative. A similar model cannot be used to describe Mn diagensis because Mn occurs in much lower concentrations than Fe and becomes rate-limiting, requiring exponential-type rate curves.

Measurements of the phase partitioning of Zn, Cu, and Cr indicate that for these elements, as for Fe, several phases can coexist in a single sediment layer. The diagenesis of Fe, especially changes in Fe hydrous oxides, influences the partitioning of these other metals in the order $Zn > Cr > Cu$.

THE CHEMISTRY OF SALT MARSH SEDIMENTS

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A series of sediment core samples were taken over a two-year period from a salt marsh in southern Delaware. Chemical analyses of pore waters and associated solid phases were made in order to examine in detail the sedimentary chemistry of iron, manganese, sulfur, and carbon.

The sediments responded primarily to the seasonal effects of temperature, evaporation, and precipitation. Variations in the observed chloride concentrations within the uppermost 20 cm were fit by an annual harmonic diffusion model. The effective sedimentary diffusion coefficient for chloride ion was calculated to be 1.1×10^{-5} $cm^2 \cdot s^{-1}$ or 0.57 times the bulk solution diffusion coefficient.

The rate of organic carbon decomposition demonstrated a zero order dependence with respect to both the organic carbon and dissolved sulfate concentrations. Organic carbon was consumed via sulfate reduction at a mean rate of 1.1×10^{-3} $mol \cdot g^{-1}$ (dry sediment) $\cdot yr^{-1}$, which yields a mean sulfate reduction rate of 5.5×10^{-4} $mol \cdot g^{-1}$ or 1.6×10^{-4} $mol \cdot cm^{-3}$ (pore H_2O) $\cdot yr^{-1}$. The net rate of pyrite production was 1.2×10^{-5} $mol \cdot g^{-1} \cdot yr^{-1}$.

Pyrite is formed as the final product of dissolved sulfide reaction with ferric oxide minerals in the sediment. It constitutes about 70-80% of the total sulfur and reactive iron inventory below 15 cm and is a potentially important reservoir for other trace metals such as Cu, Ni, Co, and Zn.

In the early summer an intense subsurface oxidation event occurs as a result O_2 infusion into the sediment through the root system of the marsh grass *Spartina*. The destruction of pyrite by this event leads to the reprecipitation of iron oxide and the release of significant quantities of sulfate and acid (H^+) into the pore waters. These oxidation products are ultimately consumed by reduction reactions and reprecipitated as iron sulfide phases during the remaining months of the year.

The regular exposure of these sediments to the atmosphere and the influence of the marsh grasses causes iron and sulfur to be cycled seasonally through oxidized ($FeOOH$, SO_4^{2-}) and reduced (FeS_2, FeS, S^0) states as decribed earlier. Were it not for this recycling mechanism, the high rate of sulfate reduction would rapidly exhaust the available sulfate supply within the uppermost sediments and prevent further organic carbon decomposition via sulfate reduction. The sediments examined in this study never became sulfate limited.

High metal oxide concentrations are maintained in the top 2 cm of sediment both by reoxidation reactions and by deposition of new material at the sediment surface. The majority of trace-metal release takes place in this zone. This dissolution process occurs by reaction of the oxides with dissolved sulfide and releases metal ions into the near-surface water pore waters from which they diffuse upward toward the sediment interface and downward into the sediment. Upon downward diffusion, Fe^{2+} precipitates first as FeS or Fe_3S_4 and is gradually converted to pyrite (conversion complete by 15 cm depth) as predicted thermodynamically. Mn^{2+} diffuses downward and precipitates as an authigenic phase. However, the exact nature of this manganese phase cannot be thermodynamically predicted due to uncertainties in free-energy data for manganese minerals ($MnCO_3$, MnS, $MnHPO_4$) and due to kinetically slow reaction rates. Both Fe^{2+} and Mn^{2+} also, diffuse upward toward the marsh surface where reoxidation reactions trap more than 93% of the iron but only 70% of the manganese. This differential loss of manganese relative to iron is believed to cause the observed depletion of manganese in the marsh sediments as compared to the adjacent estuarine sediments.

BENTHIC NUTRIENT REGENERATION AND SEDIMENT-WATER EXCHANGE
IN AN ORGANIC-RICH COASTAL SEDIMENT
CAPE LOOKOUT BIGHT, NORTH CAROLINA

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Organic-rich debris associated with high productivity in nearshore areas is de-
posited in sediments in a relatively labile state. In coastal environments where
sedimentary inputs are large, microbially-mediated benthic remineralization of
this debris may supply a significant proportion of the nutrient requirements for
primary productivity in overlying waters. A quantitative understanding of the
coupling between the sediments and overlying waters requires a knowledge of the
mechanisms controlling both nutrient remineralization rates and chemical exchange
across the sediment-water interface. This study examines the sites and rates of
benthic nutrient regeneration using sediment and interstitial water chemistry,
in situ measurements of sediment-water exchange processes, laboratory determin-
ations of *in situ* production and adsorption rates for remineralized constituents,
and kinetic and stoichiometric modeling of organic matter decomposition and early
diagenesis in an organic-rich fine-grained anoxic mud in Cape Lookout Bight, North
Carolina.

In areas of rapidly accumulating fine-grained sediments heterotrophic breakdown
processes do not exhaust the reactive fraction of the organic matter before it is
buried by subsequently deposited material. Regeneration processes may occur both
at the depositional interface prior to burial, and within the sediment column fol-
lowing burial. Consequently, the release of remineralized carbon, nitrogen and
phosphorus by the benthic system and net flux to overlying waters are the result
of both processes at the sediment-water interface and diagenetic processes within
the sediments.

Fluxes of regenerated carbon, nitrogen, and phosphorus were measured *in situ* directly
from diver emplaced benthic chambers from October 1976 to November 1978. These
flux studies demonstrated a repeated seasonal cycle in benthic exchange of nutrients
as a result of the temperature dependence of bacterial decomposition rates. Fluxes
measured for ammonium and phosphate ranged from $\sim$40 to $\sim$1200 and from $\sim$-4 to $\sim$130

μmoles.m^{-2}.h^{-1} respectively, over the observed temperature range of 5° to 27°C.

Concurrent flux studies of methane and the noble gas radon-222 allow calculation of experimentally defined apparant bulk sediment diffusivities (D_s'). During summer months both tracers yield calculated D_s' values up to 3 times above the expected molecular diffusivity. The sediments are devoid of macrofauna during this time and the elevated D_s' values are hypothesized to result from enhanced molecular diffusion associated with increased surface area and concentration gradients created by bubble tubes maintained by the ebullition of methane gas at low tide. Nutrient fluxes calculated indirectly via Fick's first law using nutrient interstitial water concentration gradients at the sediment-water interface and the tracer derived apparant diffusivities yield predictions which are compared with observed fluxes to determine the relative importance of rapid production and removal processes at the sediment-water interface in controlling nutrient sediment-water exchange.

Carbon, nitrogen and phosphorus deposited in the form of particulate organic matter is either remineralized and released back into the water column or trapped as refractory material within the sediments and buried. Mass balance calculations using observed fluxes, a sedimentation rate of 5 cm.y^{-1}, and the amount of residual nitrogen indicate that approximately 50% of the nitrogen coming into the sediment is returned to the water column. About 35% of the carbon is regenerated. Data for phosphorus are forthcoming.

Laboratory studies of the rate of nutrient remineralization within the sediment predict summertime net production rates for ammonium (corrected for adsorption) more than sufficient to account for observed summer fluxes. Over 70% of the regeneration of ammonium and phosphate occurs in the upper 12 cm of sediment. Winter production rates in the upper 2 cm are a factor of 10 lower. Bacterial numbers in the sediment remain high throughout the year ($10^{10} - 10^{11}$ cells.ml^{-1} wet sediment).

A modeling effort is just now beginning. Exponential curve fits of vertical interstitial-water concentration profiles used to calculate concentration gradients at the sediment-water interface will also allow modeling of remineralization rates and fluxes. These model predictions can be compared with observed fluxes, production

and adsorption rates, sedimentation rate, and diffusion coefficients determined
independently to test the accuracy of the diagenetic model in this environment.
Measured ΣCO_2, ammonia, and phosphate production rates, sulfate reduction rates
and budgets for carbon, nitrogen and phosphorus provide information on the stoichio-
metry of organic matter decomposition under these predominantly anaerobic conditions.

THE ROLE OF ZOOPLANKTON FECAL MATERIAL IN THE CYCLING AND DEPOSITION OF PARTICULATE MATTER IN AN ESTUARINE AND DEEP-OCEANIC REGION OF THE NORTH EASTERN PACIFIC OCEAN

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Between March 1977 and April 1978 a quantitative investigation of the cycling and deposition of particulate matter was conducted in Dabob Bay, a biologically productive estuary in Washington State. The purpose of the study was to test the hypothesis that large particle aggregates, specifically zooplankton fecal material, can dominate the processes of vertical flux in an estuary. Microscopic, gravimetric, and chemical analyses were performed on suspended particulate matter collected by filtration, net hauls, and sediment traps and on bottom sediments collected by box and gravity corers. The sediment traps containing preservative were moored for periods of 21 to 49 days at depths of 55-60 m, well below the 5-20 m thick euphotic zone and above the bottom depth of 112 m. Since the annual vertical flux of 1.2 dpm cm^{-2} yr^{-1} unsupported ^{210}Pb measured by the sediment traps was similar to the 0.9 to 1.1 dpm cm^{-2} yr^{-1} steady state depositional flux of unsupported ^{210}Pb determined from four cores of the underlying sediments, the traps appeared to sample representatively settling particulate matter.

Over an annual period, zooplankton fecal pellets containing particles of both biogenous and abiogenous origin accounted for 38% of the dry matter collected by the sediment traps. However, disintegration of large particles during subsampling the traps was apparent, and it is estimated fecal pellets actually comprised 54 to 99% of the trapped sediment. The vertical flux of fecal pellets per cm^2 per day averaged 104 in the spring and summer, 209 in the fall, and 298 in the winter. These fluxes combined with the abundances of adult zooplankton yield average fecal pellet production rates per individual zooplankton per day of 5 in the spring and summer, 12 in the fall, and 27 in the winter. The low production rates of spring through fall occurred when zooplankton abundances were high relative to winter and are believed to reflect fecal pellets being eaten and re-eaten a number of times (i.e., recycled) before settling into the sediment traps. Settling particulate matter exhibited rather uniform deposition rates and chemical composition in the spring and summer, caused, at least in part, by the prevalent reutilization of

of zooplankton fecal pellets. Trapped sediment during this period contained 22
to 26% dry weight organic matter, which was sedimenting at 44 to 64 $\mu g\ cm^{-2}\ day^{-1}$.
Aluminosilicates comprised 43 to 61% of the collected dry matter and were settling
from 111 to 147 $\mu g\ cm^{-2}\ day^{-1}$. Reflecting a fall phytoplankton bloom, the deposi-
tion rate of organic matter rose to 86 to 102 $\mu g\ cm^{-2}\ day^{-1}$ during fall. The alu-
minosilicate sample fraction and deposition rate both approximately doubled in
late fall, as a consequence of the seasonal increase in precipitation and terre-
strial runoff. The winter sediment trap collections displayed the lowest organic
matter contribution of 8 to 16% dry weight and the highest aluminosilicate content
of 63 to 85% dry weight. The high fecal pellet production rate per individual
zooplankton in winter suggests little reutilization, which was evident in the highly
variable deposition rates of organic matter, 28 to 46 $\mu g\ cm^{-2}\ day^{-1}$, and alumino-
silicates, 132 to 447 $\mu g\ cm^{-2}\ day^{-1}$.

The residence times of particulate aluminum and carbon in the euphotic zone were
calculated from the average suspended particulate concentrations in the euphotic
zone and the deposition rates measured by the sediment traps. The residence times
for aluminum were relatively constant throughout the year and averaged 2 days. The
lack of significant runoff into Dabob Bay in the summer and the short residence
time for aluminum requires another source of aluminum during that season. It is
believed that clays deposited in shallow regions during the high runoff and predom-
inately southerly winds of winter are resuspended and introduced into the mixed
layer by tides and the northerly winds of summer. Near secular equilibrium values
for polonium-210 and lead-210 in the summer sediment trap samples and bottom sedi-
ments indicate a resuspended origin for aluminosilicates. Winter sediment trap
collections had polonium-210 to lead-210 ratios of 0.5 to 0.7, similar to the 0.6
to 0.9 measured in Puget Sound area riverborne particulate matter. This disequili-
brium implies the trapped sediments of winter were recently derived from terrestrial
runoff. The residence times for carbon were 8 to 12 days during spring through
fall and twice that in the winter. The higher loss rates of carbon from the euphotic
zone during spring, summer, and fall relative to winter appear to be due to increased
predation among the more abundant zooplankton of those seasons.

Sediment trap derived deposition rates for selected elements were also compared

with recent accumulation rates in the bottom sediments. The bottom accumulation rates were determined by lead-210 geochronology with corrections applied for sediment mixing. Bottom accumulation rates for aluminum (6.0 mg cm^{-2} yr^{-1}), iron (3.6 mg cm^{-2} yr^{-1}), and chromium (8.1 μg cm^{-2} yr^{-1}) were within experimental error identical to the sediment trap deposition rates. However, sediment trap deposition rates for carbon (7.4 mg cm^{-2} yr^{-1}), manganese (0.2 mg cm^{-2} yr^{-1}), and arsenic (1.1 μg cm^{-2} yr^{-1}) were 308%, 338%, and 189% respectively of their accumulation rates into the bottom sediments. The excess carbon flux can be accounted for by previously measured benthic respiration rates. The vertical sediment profiles of manganese and arsenic indicate the manganese and possible arsenic are diffusing out of the bottom.

These results indicate zooplankton fecal material can serve as a significant vertical transport agent for organic and inorganic particulate matter in an estuarine environment. In addition, the feeding activities of zooplankton exert considerable influence on the residence time of particles in the euphotic zone and affect the chemical composition and the temporal variability of the particulate flux falling to greater depths.

Note: Bottom sediments, suspended particulate matter from the euphotic zone, and sediment trap collections from depths to 3000 m were collected in the northeastern Pacific Ocean in June, 1978. Experimental work on these data are presently being completed, and the results should be in presentable form by October, 1979.

SESSION III

TRACE ELEMENT BIOGEOCHEMISTRY

THE DISTRIBUTIONS OF MANGANESE IN THE PACIFIC OCEAN
AND SEVERAL METALS IN PELAGIC PORE WATERS

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This thesis is comprised of two main papers: "The Distribution of Manganese in the Pacific Ocean" and "Metal Distributions in the Pore Waters of Carbonaceous Pelagic Sediments." In addition, Mn concentrations are presented for bottom and vent waters from the Galapagos Rift and several locations along the East Pacific Rise. Two new analytical procedures were developed to make these seawater Mn and pore-water metal measurements. These methods are documented in this thesis.

This report presents the vertical distributions of "total dissolvable manganese" at 13 stations in the Pacific. Surface-water values range from about 3 nmol/kg to about 0.3 nmol/kg. The surface concentrations show a general correlation with lead-210, suggesting that the major source of manganese to the surface waters of the Pacific is desorption from atmospheric particulates. The residence time of Mn in surface waters is 5 to 25 years. The highest Mn concentrations in subsurface waters are often found in the oxygen minimum. This maximum in the O_2 minimum is believed to originate either as reduction of Mn solids in nearshore sediments and subsequent advection or by seawater equilibrium with a metastable oxide similar to hausmannite (Mn_3O_4).

Concentrations of Mn, Fe, Cu, Ni, Cd and Zn in the pore waters of carbonaceous pelagic sediments have been measured for two sites in the eastern equatorial Pacific. Concentrations of Mn, Cu and Ni are also presented for two locations in the eastern equatorial Atlantic. The results from these four sites suggest that the distributions of the trace metals (Cd, Cu, Ni and Zn) are determined by processes affecting the major oxidants (O_2, NO_3^-, Mn and Fe oxides). Dissolved cadmium, zinc and copper concentrations in the top 2 cm of sediment are 3 to 8 times bottom water. These gradients predict benthic fluxes which may be important in the oceanic budgets of these elements. Manganese, nickel and iron concentrations near the interface are essentially the same as bottom water.

The concentrations of nickel in the Mn reduction zone reach levels up to 40 times that of bottom water. This nickel gradient drives a flux into the Mn oxidation zone which is large enough to influence the nickel abundance of the bulk sediment. Dissolved manganese concentrations range from 10 nmol/kg^{-1} in the oxygenated zone to 100 μmol/kg^{-1} down core. The maximum Mn concentrations observed agree with those predicted by saturation with rhodochrosite if this equilibrium readjusts to 1 atm pressure in several hours or less.

BEHAVIORS OF MANGANESE, IRON AND ALUMINUM IN THE OCEAN

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The behavior of particulate matter in the ocean and the mechanism of removal of chemical elements from seawater were studied in both coastal and open seas. Thermodynamically stable forms of manganese, iron and aluminum in seawater were calculated to be solid phases. These elements in settling particles, suspended particles and seawater were determined and compared with their compositions.

The sediment traps were deployed 13 times from August 1976 to January 1978 in coastal sea, Funka Bay (92 m deep), Japan, and also deployed from July to August 1978 (31.3 days) in the northern North Pacific (5.30 km). The results are summarized as follows.

In the coastal sea, Funka Bay:

1) The total particulate flux in winter ($9.92-23.40$ $g/m^2/day$) was very much larger than that in summer ($0.51-2.86$ $g/m^2/day$) and also larger than the sedimentation rate (2.60 $g/m^2/day$) estimated from the Pb-210 method.

2) The concentration of aluminum in settling particles that were collected in the sediment trap was larger than that of suspended particles collected by filtering of seawater. This may be due to either the addition of large terrestrial particles to the sediment trap samples or the degraded biogenic particles contained in the trap.

3) The concentration of manganese in the near-bottom water increased with time during summer when the water was stagnant. The flux of manganese from the bottom to water was calculated to be 3 $mg/m^2/day$ from the increment of manganese in the water. The directly observed downward flux of manganese was $1.3-4.5$ $mg/m^2/day$ at the 80 m deep. Most of the manganese reaching to the bottom is regenerated.

In the open ocean:

4) The total particulate fluxes in the abyssal waters (1.1, 2.2 and 4.4 km deep) were 0.150-0.210 $g/m^2/day$ and seemed to decrease with depth. The flux at a layer 50 m above the bottom (5.25 km deep) was only 0.034 $g/m^2/day$, but the fluxes of these elements were not small. On the contrary, to the total flux, the flux of manganese obviously increased with depth. This may be caused by the regenerated manganese at the near bottom.

5) The suspended particles contained greater amounts of organic matter, and the insoluble elements in the particles increased with depth. The settling particles may be diluted with biogenic silicate and calcium carbonate particles in a highly productive area such as the northern North Pacific.

Based on these results and other information, the following conclusion was reached. The aggregate of suspended particles is important as a conveyer of insoluble trace elements from the surface to the abyss, and the formation of solid phases in seawater is not the rate-determining step for the removal of these elements from the ocean.

MARINE PHOSPHORUS GEOCHEMISTRY

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The primary purpose of this work is to quantify some aspects of the marine phosphorus cycle. Investigations centered on two primary areas: (1) interstitial concentrations of nutrients and nutrient-related constituents were measured in marine sediments to identify the reactions controlling interstitial nutrient concentrations; and (2) accumulation rates of organic and various inorganic phosphorus phases were measured in marine sediments to help elucidate the primary phosphorus sinks in today's oceans.

Interstitial concentrations of $total-CO_2$, pH, PO_4^{3-}, NO_3^- plus NO_2^-, SO_4^{2-}, S^{2-}, Fe^{2+} and Mn^{2+} from sediment cores in the eastern equatorial Atlantic demonstrated that oxidants are consumed in order of decreasing energy production per mole of organic carbon oxidized (O_2 > manganese oxides $\sim$nitrate >iron oxides >sulfate). $T-CO_2$ concentrations reflect organic regeneration and calcite dissolution. Phosphate profiles are consistent with organic regeneration and with uptake and release during inorganic reactions. Nitrate profiles reflect organic regeneration and nitrate reduction. The estimated benthic flux of nitrate to the ocean is small from pelagic sediments, but denitrification rates may be globally significant. Dissolved iron and manganese profiles suggest reduction of the solid oxide phases, upward fluxes of dissolved metals and subsequent entrapment in the sediment column. Sulfate is constant and sulfide is absent, reflecting the absence of strongly anoxic conditions.

Accumulation rates of phosphorus, iron and manganese were measured in cores from the crest and flanks of the East Pacific Rise and the Bauer Deep. Phosphorus is being deposited about 20 times faster in metalliferous sediments near the Rise crest than in adjacent flank deposits, and about 40 times faster on the crest than in the Bauer Deep. Almost all the phosphorus is associated with hydrothermally derived iron oxyhydroxides, and is derived by sorption from seawater.

A mass balance for phosphate in the oceans was constructed, based on measured accumulation rates of various phosphorus constituents in the eastern equatorial Atlantic,

plus extensive information from the literature. The results indicate that:
(1) the river input of reactive phosphate is **poorly** known; and (2) 90% of the identified removal of reactive phosphorus from the oceans occurs by burial in biogenic phases: organic phosphorus, calcium carbonate phosphorus and phosphorites. The remaining 10% is buried with metalliferous sediments. Burial of authigenic iron and aluminum phosphates is probably unimportant, but burial of clay-sorbed-P is presently unquantified and could be significant.

A new analytical technique for measuring organic carbon in marine sediments was developed. The technique relies on carbonate removal by sonication with H_3PO_4, and analysis of both the solid and dissolved residues for carbon. The technique is free from carbonate interferences, suffers no losses due to acid solubilization and has excellent precision and accuracy.

A method was developed to correct for a systematic absorbance error in the automated colorimetric measurement of reactive phosphate inherent in the curved flow-cells employed in Technicon Auto Analyzer colorimeters.

THE MARINE BUDGETS OF SILICA AND ^{32}SI

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The study of the marine budgets of silica and the cosmogenically produced iso-
tope, ^{32}Si, has been approached in this thesis with the aid of natural radionu-
clide chronometers including ^{210}Pb, ^{14}C, ^{231}Pa and ^{230}Th. Rivers are the primary
source of marine silica, whereas direct atmospheric precipitation supplies the
majority of the ^{32}Si to the oceans. Although biogenic and inorganic removal of
these silicon isotopes has been postulated, this study affirms the primary impor-
tance of marine organisms by assessing the flux of biogenic silica into various
oceanic repositories.

The biogenic silica content of marine sediments is determined using a 5 hour, 85°C.,
1% Na_2CO_3 extraction solution. The leaching solution is sampled after 1, 2, 3, and
5 hours so that a correction can be made for the amount of silica extracted from co-
existing clay minerals.

Accumulation rates of biogenic silica in continental margin sediments are established
using excess ^{210}Pb and varve chronologies. Coupling these chronologies with ^{32}Si
measurements in a Gulf of California sediment core yields a ^{32}Si half life of 276 ±
32 years. ^{14}C depth profiles in the organic-rich sediments from Carmen Basin, Gulf
of California, and Walvis Bay, South Africa, cannot be used to establish sediment
accumulation rates because these profiles are predominantly controlled by variations
in the intensity of upwelling or the rate of air-sea gas exchange.

In the deep-sea, the effects of biological mixing on the distribution of chronologi-
cal tracers are established by measuring ^{210}Pb and ^{32}Si activities in the near inter-
face deposits. Eddy diffusion appears to be a reasonable analogue to the deep-sea
particle mixing processes as mixed layer radionuclide profiles can be fit to steady
state diffusion-advection equations. Deep-sea mixing coefficients determined in
this study range between 20 and 200 cm^2/ky. ^{226}Ra, ^{231}Pa, and ^{230}Th data in deep-
sea sediments indicate that these deposits are typically mixed to a depth of 7 to 15
centimeters.

Biogenic silica accumulation rates in Antarctic deep-sea sediments are established from the biostratigraphy of the radiolarian, *Cycladophora davisiana*. The utility of this biostratigraphic method is confirmed using [231]Pa and [230]Th dating methods. Radiochemical and biostratigraphic data indicate that the siliceous sediments beneath the south Atlantic Antarctic Convergence accumulate as rapidly as 50 cm/ky. Although these rapidly accumulating sediments in the south Atlantic cover only 10% of the area occupied by Antarctic siliceous sediments, they account for 36% of the total biogenic silica removed in Antarctic deposits.

Combining radiochemical, biostatigraphic, and biogenic silica data from continental margin and deep-sea sediments indicates that most marine silica removal is biogenic and occurs in the deep-sea sediments surrounding Antarctica. Secondary repositories of marine silica include estuarine sediments as well as sediments beneath the Bering Sea, the North Pacific Ocean, and the Sea of Okhotsk. Although upwelling areas such as the Gulf of California, the Peru-Chile coast, and Walvis Bay sustain some of the highest rates of silica accumulation in the marine environment, these sediments are confined to such small areas that they account for less than 10% of the overall marine silica removal. Within the uncertainties of the measurements, the calculated rate of biogenic silica accumulation in oceanic sediments balances the rate of riverine silica supply.

The oceanic repositories of [32]Si are established by coupling [32]Si measurements with biogenic silica accumulation rates. Most of the [32]Si supplied to the oceans is removed by *in situ* radioactive decay with only 5% incorporated into the sediment column. Theoretically, the repositories of [32]Si and silica can be separated in the marine environment by the interaction of sedimentation, dissolution, and sediment mixing. This decoupling process for silica and [32]Si, however, is only important in very slowly accumulating siliceous sediments in which the diffusive flux of silica from the sediment is much greater than the long-term silica accumulation rate. As most marine silica is removed in rapidly accumulating deposits, the major [32]Si repositories coincide with the major silica repositories.

Measurements of [230]Th and [231]Pa in rapidly accumulating siliceous sediments beneath the south Atlantic Antarctic Convergence show [230]Th/[231]Pa activity ratios as low as 2 relative to the sea water production ratio of 10.7. It can be concluded from

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these data that ^{231}Pa is being preferentially deposited relative to ^{230}Th in these sediments. The ^{230}Th and ^{231}Pa inventories in these rapidly accumulating siliceous sediments are as much as 6 to 14 times greater than the inventories predicted from the uranium in the overlying water column.

THE HETEROGENEOUS KINETICS OF SILICA DISSOLUTION IN AQUEOUS MEDIA

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A major control of the geochemical cycles of many elements involves the transfer of the element across a solid-liquid interface. The chemical weathering of rocks by aqueous solutions and the chemical precipitation of minerals in sedimentary environments are two important examples involving transfer across a solid-liquid interface. In many environments, especially those with low temperature, the time dependence of this transfer may be regulated by chemical reactions, as opposed to hydrodynamic transport. The rates of chemically controlled reactions involving transport across a solid-liquid interface are poorly understood, both from experimental and theoretical points of view.

The cycle of silica in the oceans and marine sediments has received more attention, from an accounting standpoint, than from a physical chemical perspective. Marine chemists and geochemists have long realized that a chemical kinetics description is important for understanding the chemistry of silica in marine and sedimentary environments. The dissolution of biogenic opal in the ocean, the stability and preservation of opaline microfossils in sediments, and the maturation of opal to chert are three important processes that require a more thorough understanding of the kinetic controls of silica dissolution and precipitation reactions.

A review of the chemistry of silica, with special emphasis on dissolution and precipitation kinetics of silica, is presented. The surface chemistry of silica, with respect to surface acidity and adsorption of metal ions, is introduced. An experimental program designed to examine the effect of solution components on the initial kinetics of silica dissolution is described. The results of this program are analyzed in terms of the surface chemistry of silica. The form of the rate-determining step of silica dissolution is elucidated. The rate constant for silica dissolution may be expressed in terms of excess surface hydroxide in NaCl media. A theory for the kinetic stability of silica surfaces is proposed.

Implications of the experimental program to chemical processes in natural systems (including the dissolution of diatoms, the maturation of opal to chert, and the weathering of rocks) are suggested.

The application of the experimental program design to other simple oxide systems might be interesting.

VARIABLE INFLUENCE OF THE ATMOSPHERIC FLUX ON THE
TRACE-METAL CHEMISTRY OF OCEANIC SUSPENDED MATTER

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The particulate concentrations of 17 trace metals, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Sb, Au, Hg, Pb and Th were measured in the marine atmosphere (58 samples) and in the deep waters (35 samples) of the tropical North Atlantic. For oceanic suspended matter, the results are similar to those in samples from the Atlantic and the Pacific oceans collected during the GEOSECS program. Based on these results, a flux balance was made for the mixed layer between input via the atmosphere and removal through small and large particles. These data show that the primary flux of suspended aluminosilicates in the tropical North Atlantic is attributable to the atmospheric input. Elements Sc, Th, Fe, V, Mn, Co and Cr show high correlation with Al in the marine atmosphere. Of these elements, Fe, Mn, V, Co and Cr are influenced by additional processes, such as biological, in the marine environment. For elements Ni, Cu, Zn, Se, Ag, Sb, Au, Hg and Pb, high enrichments were observed (relative to average crustal material) in the marine atmosphere which may be due, at least partially, to the influence of anthropogenic sources. These metals also show similar enrichments in deep-ocean suspended matter. Model calculations indicate that the atmospheric flux may not control the deep-ocean particulate chemistry of Ni, Cu, Zn, Ag, Sb, Au and Hg. Hence, it is likely that, for these elements, the enrichment in the ocean is due to processes within the marine regime, for example, their involvement in the biological cycle of the ocean. For Se and Pb, the atmospheric source appears to be the dominant contribution to their particulate concentration in seawater. In the deep North Atlantic, particulate Pb appears to be mostly of anthropogenic origin, which is not the case for Se.

TRACE ELEMENT CHEMISTRY OF AGING MARINE DETRITUS DERIVED FROM COASTAL MACROPHYTES

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Macrophytes, the dominant primary producers of the coastal ocean, introduce enormous quantities of organic matter into the marine detrital pool. Decomposing organic matter undergoes complex orthochemical and microbially mediated transformation which prefigure a dynamic trace-element chemistry. This research is a laboratory study of the chemistry of aluminum, iron, manganese, copper, silver, zinc, and cadmium in microbially aged detritus derived from nine species of estuarine macrophytes representing salt marsh, seagrass, seaweed, and mangrove ecosystems.

Aging detritus usually accumulated these metals on both a concentration and an absolute basis. Conversely, because of its peculiar redox chemistry, manganese was lost from decomposing detritus. Rapid decomposition of easily degraded macrophyte material (e.g., seaweeds) suppressed or prevented accumulation of all metals studied except copper. Consequently, decay-resistant vascular plant detritus bound metals more efficiently than seaweed detritus. As vascular plant detritus ages, elevated amounts of bioavailable trace elements may be introduced into detritus-based food chains.

Microbes affect the trace-element chemistry of macrophyte detritus by chemically altering the organic substrate. Only a small fraction of the metal accumulation was in the microbes themselves. In fact, microbial colonization inhibited accumulation of some elements. Generally, accumulation was favored significantly more by aerobic than by anaerobic decomposition.

Macrophyte detritus decomposition has considerable potential for affecting the minor and trace-element chemistry of estuarine waters. Decomposing macrophyte material releases manganese and scavenges many other elements. The chemistry of waters dominated by macroalgal production and decay may be quite different from that of a seagrass or mangrove habitat.

THE ROLE OF PHYTOPLANKTON AND PARTICULATE ORGANIC CARBON IN TRACE METAL DEPOSITION IN LONG ISLAND SOUND

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The role of phytoplankton as a carrier phase for removal of Fe, Mn, Cu, Cd, Zn, Ni, Co and Pb in the open areas of Long Island Sound, USA, has been evaluated. Metal concentrations in the phytoplankton were found to be relatively constant seasonally and spatially and did not depend on the species composition of the phytoplankton assemblage. Metal concentrations in the plankton are similar to concentrations reported for other areas with the exception of Cd which is lower and Mn which is higher. Iron and Mn concentrations show the greatest seasonal variability and are high in winter and summer, respectively. The concentration of Cu, Fe, Cd, Pb, Zn in the plankton correlates with the nitrogen content of the plankton assemblage. Sediment samples were analyzed for nitric-acid leach-able metals, organic carbon, cation exchange capacity and grain-size distribution. Metal distributions and concentrations are similar to those previously reported for Long Island Sound sediments. Cadmium concentrations are 200 times higher in western LIS than in the eastern regions. Sedimentary organic carbon concentrations and cation exchange capacity increase from east to west, towards the Connecticut and New York shores, as do the metal concentrations. Within the total data set, organic carbon and grain size are highly correlated with metals. Removal of sandy samples from the data set causes the correlations between the metals Fe, Pb, Mn, Zn, C, Cu and Ni and organic carbon to decrease slightly, while the correlations between these metals, grain-size distribution, sample depth, Fe and Mn significantly decrease. Cobalt is poorly correlated to all variables. Multivariant statistical analysis using organic carbon, grain-size distribution, sample depth, Fe and Mn concentrations as independent variables does not significantly improve the explained variance between organic carbon and Cu, Pb, Zn, Fe and cation exchange capacity. The similarity between organic carbon and trace-metal distributions coupled with the low correlations between the trace metals, grain-size distribution and other major sedimentary phases represented by Fe and Mn, argues that trace-metal distributions (except Co and possibly Ni) in muddy sediments from Long Island Sound are regulated principally by organic carbon. The cation exchange capacity of the sedi-

ments is also controlled by organic carbon. The cation exchange capacity of sedi-
mentary organic carbon is ∿6.4 meq/g organic carbon or ∿2.0 meq/g of organic matter.
Budgets comparing the annual incorporation of metal into plankton to that deposited
in sediments indicate that plankton may play a significant role in removing trace
metals to the sediments of Long Island Sound. Metal:metal ratios in the plankton
and sediments of Long Island Sound are similar, indicating coupling between the
plankton and sedimentary metal distributions. A method for evaluating the adsorp-
tion capacity of various plants was developed. The adsorption capacity of natural
phytoplankton assemblages, a variety of macrophytes, zooplankton and particulate
matter was found to be $0.22 \pm .05$ meq/g, 0.5 to 1.5 meq/g, $1.7 \pm .5$ meq/g and 0.27
$\pm .10$ meq/g, respectively. The macrophyte species and condition of the plant in-
fluence the adsorption capacity. Plants that had been partially degraded had ad-
sorption capacities near 0.3 meq/g. The adsorption capacities of these plants are
similar to those of most clay minerals and other colloidal solids found in seawater.
Adsorption of Cu from seawater by phytoplankton is shown to be a minor process in
the geochemical cycle of Cu, and probably does not greatly influence Cu concentra-
tions observed in plankton.

SESSION IV

TRACE GASES AND NUTRIENT CYCLING

GEOCHEMISTRY OF DISSOLVED GASES IN THE HYPERSALINE ORCA BASIN

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An understanding of anaerobic decomposition processes is important to marine geochemists. Chemical changes that lead to the development of anoxic conditions are of interest beyond the immediate confines of the stagnating waters in basins and fjords where they are studied. The sequence of oxygen depletion, followed by nitrate, nitrite, and sulfate reduction is an oft repeated pattern in anoxic marine sediments. During anaerobic decomposition, organic material [represented here as $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$] is decomposed into the nutrient H_3PO_4 and the dissolved gases CO_2, CH_4, NH_3, N_2, and H_2S.

The spatial distributions of dissolved gases have been measured in the anoxic Orca Basin (26°55'N, 90°20'W) in order to investigate the influence of hypersaline conditions on anaerobic decomposition processes. Dissolved gas production is evidenced here by the fact that the isolated Orca Basin brine is supersaturated with dissolved gases. When a sample is brought to the surface, the water effervesces, releasing gas bubbles with a composition of 63.7% N_2, 34.6% CH_4, 1.1% Ar, and 0.6% CO_2. This degassing effect forced the use of a pressurized sampling device in order to obtain representative brine samples for gas chromatographic and mass spectrometer analyses. The gases that have been measured are oxygen, argon, nitrogen, carbon dioxide, methane, ethane, propane, nitrous oxide, hydrogen sulfide, and ammonia. Measurements of helium, xenon, krypton, and xenon are in progress.

Dissolved oxygen was completely absent in the basin, as were nitrate and nitrite. Sulfate and carbon dioxide are the primary oxidizing agents, except at the brine-sea water interface where oxygen, nitrate and nitrite are present. Nitrogen gas concentrations averaged 500 μM with argon levels of 16 μM. The N_2/Ar ratio of 37 is approximately the average value of normal seawater and indicates that no measureable N_2 production is taking place in the brine. Methane levels in the brine were generally higher than 700 μM. These concentrations are higher than those found in any other marine waters. Methane produced in the brine is trapped

there due to the density gradient between the brine and the overlying Gulf water. Ethane (1.0 μM) is also higher in the brine than in the overlying water and is probably produced biogenically along with methane. The heavier $\delta^{13}C$ of the methane in the brine (-73.5 °/oo vs PDB standard), as compared with sediment methane values (-85 to -105 °/oo), suggests that methane is being consumed during sulfate reduction in the sediments near the sediment-water interface. The surviving heavier methane then diffuses out into the overlying brine. Maxima in methane and ethane profiles just above the brine-seawater interface were associated with increased microbial biomass at the beginning of the deep pycnocline. These maxima probably result from degradation of particles which are not dense enough to settle immediately into the brine.

Hydrogen sulfide in the brine was absent as free H_2S, except near the interface where the concentration was 2.8 μM. The concentration of iron (~30 μM) causes the removal of most sulfide from the brine as iron sulfides, with a high density of particulate FeS being found in the water column and sediment. Since the Orca Basin differs only in salt content from other marine, anoxic areas (which have higher sulfide concentrations), the high salt concentrations must contribute to this effect. Either the reaction kinetics of iron sulfide precipitation are more favorable under hypersaline conditions or the rate of $S^=$ production (by salt-inhibited sulfate-reducing bacteria) is slower in the Orca Basin than in other anoxic, marine basins. Both of these possibilities are being examined in conjunction with the dissolved gas data.

The carbonate system in the Orca Basin is strongly influenced by carbon dioxide production during decomposition, as well as by the increased salt levels. Total carbon dioxide (both calculated from titration data and measured by gas chromatography) is greater than alkalinity (TA = 4.75 meq/L) due to microbial production of CO_2 in the brine. The carbonate system in the Orca Basin can be compared to the carbonate interactions in Dead Sea brine, an evaporite brine in the Middle East. Both pH (6.83) and ΣCO_2 (5.0 mM) in the Orca brine are higher than in Dead Sea brine (pH = 5.9 - 6.5, ΣCO_2 = 2.53 - 2.59 mM). Carbonate interactions in the Dead Sea brine are strongly influenced by its bulk ion composition, especially the Mg and Ca enrichments, 2.8 and 3.7 times, respectively, relative to normal seawater. These enrichments cause a large increase in the second dissociation

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there due to the density gradient between the brine and the overlying Gulf water. Ethane (1.0 μM) is also higher in the brine than in the overlying water and is probably produced biogenically along with methane. The heavier $\delta^{13}C$ of the methane in the brine (-73.5 °/oo vs PDB standard), as compared with sediment methane values (-85 to -105 °/oo), suggests that methane is being consumed during sulfate reduction in the sediments near the sediment-water interface. The surviving heavier methane then diffuses out into the overlying brine. Maxima in methane and ethane profiles just above the brine-seawater interface were associated with increased microbial biomass at the beginning of the deep pycnocline. These maxima probably result from degradation of particles which are not dense enough to settle immediately into the brine.

Hydrogen sulfide in the brine was absent as free H_2S, except near the interface where the concentration was 2.8 μM. The concentration of iron (~30 μM) causes the removal of most sulfide from the brine as iron sulfides, with a high density of particulate FeS being found in the water column and sediment. Since the Orca Basin differs only in salt content from other marine, anoxic areas (which have higher sulfide concentrations), the high salt concentrations must contribute to this effect. Either the reaction kinetics of iron sulfide precipitation are more favorable under hypersaline conditions or the rate of $S^=$ production (by salt-inhibited sulfate-reducing bacteria) is slower in the Orca Basin than in other anoxic, marine basins. Both of these possibilities are being examined in conjunction with the dissolved gas data.

The carbonate system in the Orca Basin is strongly influenced by carbon dioxide production during decomposition, as well as by the increased salt levels. Total carbon dioxide (both calculated from titration data and measured by gas chromatography) is greater than alkalinity (TA = 4.75 meq/L) due to microbial production of CO_2 in the brine. The carbonate system in the Orca Basin can be compared to the carbonate interactions in Dead Sea brine, an evaporite brine in the Middle East. Both pH (6.83) and ΣCO_2 (5.0 mM) in the Orca brine are higher than in Dead Sea brine (pH = 5.9 - 6.5, ΣCO_2 = 2.53 - 2.59 mM). Carbonate interactions in the Dead Sea brine are strongly influenced by its bulk ion composition, especially the Mg and Ca enrichments, 2.8 and 3.7 times, respectively, relative to normal seawater. These enrichments cause a large increase in the second dissociation

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constant of carbon acid ($pK_2' = 6.23$). The Orca Basin, however, is relatively depleted in Mg and Ca, with a carbonate system that resembles a NaCl saturated sea water ($pK_1' = 5.5$, $pK_2' = 8.3$). The low pH in the Dead Sea can be attributed to ion paring of $MgCO_3^o$. Carbonate interactions in the Orca Basin, however, are explained by the increased NaCl effect on the dissociation constants, with pH being largely controlled by the input of biogenic CO_2.

INVESTIGATION OF SURFACE MICROLAYERS IN THE DAMARISCOTTA RIVER ESTUARY, MAINE

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Information concerning the chemistry of surface microlayers has been derived primarily from studies of short duration, often conducted in response to suspected surface contamination. The intent of this thesis is to provide information from an uncontaminated system covering seasonal and spatial variations. The thesis considers both chemical and biological materials in terms of their distributions in the microlayer and bulk water phases. The chemical analyses have tended to dominate, with the anticipation that the biology will in some ways reflect the chemical nature of the microlayer.

The microlayers have been characterized chemically by monitoring the relative amounts, in the microlayer and bulk waters, of dissolved inorganic nutrients and dissolved and particulate organic material. Most of the analyses have been conducted during one full seasonal cycle. The nutrient analyses have a two-year record while some of the more specific organic material investigations are being conducted during this final spring-summer season. Four locations are sampled regularly in the estuary. An offshore station, representative of Gulf of Maine water, is also monitored to discriminate primarily estuarine influences. Other samples reflect transient surface and bulk water events, such as surface slicks, foam lines, or localized phytoplankton blooms. The samples have covered a variety of meteorological conditions. Sampling the microlayers over tidal cycles and 24-hour time periods has yielded most interesting information and will be continued intensely this summer.

Nutrient enrichments on the surface microlayers have been reported. Small but consistent and significant enrichments of phosphate and nitrite have been found. The enrichments seem insensitive to surface roughness below Beaufort 5 surface conditions. Bubble absorbtion may not be a primary reason for the phosphate enrichment. The nitrite enrichment has not been previously reported. The microlayer microbiota may be important in these enrichments and are being investigated further. Contrary to previous reports, the results do not show a significant nitrate enrichment

relative to the bulk water. The nitrate concentrations in the microlayer are occasionally significantly different from those in the bulk water, but the micro-layer is just as likely to be depleted as enriched. The addition of ammonia and total organic nitrogen analyses may aid in understanding the microlayer nitrogen system.

The surface microlayers have usually been reported to be organically enriched. Consistent quantitative data are missing, however, and considerable disagreement exists concerning the primary classes of microlayer material. Also found was consistent enrichment of dissolved organic material (DOM) in the microlayer, along with many complexities. While microlayer DOM values generally follow bulk water values over the seasonal cycle, there is a suggestion of an inverse relationship whereby, over short intervals, peak values of microlayer DOM are associated with minimal values of bulk water DOM. Microlayer DOM concentrations are often 2 or 3 times as great as bulk water values without development of visible slick conditions. On the other hand, dense slicks may often have relatively low DOM values. Areas of the surface have been isolated in order to remove microlayer material and to assess resupply of material from the bulk water. Inclusion of microlayer DOM has permitted consideration of a more complete DOM budget for a tidal cove and for the whole estuary.

The dissolved organic material has been analysed by both wet oxidation TOC and by UV absorbance methods and some qualitative information is becoming available. Or-ganic nitrogen and phosphorous analyses and carbohydrate measurements have been added in an attempt to classify further the microlayer material.

A thorough comparison of sampling devices was critical to the thesis. This has resulted in the ability to sample at depths from 50 to 500 μm in the microlayer. From this work has come support for an earlier suggestion that the layer of dis-solved organic enrichment may be relatively thick.

The picture of microlayer chemistry emerging is intriguing and the biological chemi-cal interactions are even more confusing. The final summer's work is intended to consider more carefully some of the questions so far raised.

GEOCHEMISTRY OF INORGANIC NITROGEN COMPOUNDS IN TWO MARINE ENVIRONMENTS: THE SANTA BARBARA BASIN AND THE OCEAN OFF PERU

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This study is concerned with processes related to the marine nitrogen cycle, namely denitrification, nitrification and nutrient regeneration, in two eastern boundary regions of the Pacific Ocean: Santa Barbara Basin off southern California and the ocean off Peru. Data were obtained for the distribution of the inorganic nitrogen compounds, namely, nitrate, nitrite, nitrous oxide and ammonia, as well as the $\delta^{15}N$ values of the combined nitrate and nitrite in the water column. In both areas, primary productivity is high due to upwelling, and denitrification is developed in the anoxic bottom water of the former area and in the subsurface oxygen-deficient zone of the latter area.

More than 300 water samples were retrieved from the Santa Barbara Basin and several adjacent areas off southern California on seven cruises between 1975 and 1978. It was observed in the bottom water of Santa Barbara Basin during normal non-flushing conditions, that nitrate was depleted (up to 18 μM deficit) but enriched in ^{15}N by 1 to 8 °$/_{oo}$ relative to the nitrate in the overlying seawater, while phosphate was enriched (up to 1 μM in excess). When well developed, the denitrifying zone was marked by a sharp increase of nitrite or a sharp decrease of N_2O. Its thickness was estimated to be 20-40 m. During the August 1978 cruise, N_2O was found to be 12% supersaturated in the surface water, which corresponds to a flux of 120 μmol cm^{-2} yr^{-1}. Below the mixing zone, nitrate and N_2O were linearly related with a slope of 310:1, which suggests that 0.3% of regenerated nitrogen nutrients are converted to N_2O during nitrification. At the sill depth, N_2O was 300% supersaturated, whereas in the bottom water, N_2O was 75-90% undersaturated, most probably due to consumption by denitrifying bacteria.

Flushing of the basin water in the Santa Barbara Basin, similar to that reported by Sholkovitz and Gieskes (1971), was observed between April and August 1977. During normal conditions, minor disturbance of the Basin water, as indicated by nitrate and phosphate distributions, was also observed several times, which supports Sholkovitz's hypothesis (1972) of a frequent input of smaller quantities of

new water. The distribution of temperature and nitrate in the Santa Barbara Basin was carefully simulated using mathematical models. The results strongly suggest that horizontal transport is as important as vertical transport. The parameters evaluated in the model calculation were used to determine the fluxes in oxygen, nitrate and phosphate. The total consumption of nitrate in the basin water during denitrification was determined to be 1.2×10^9 - 2.5×10^9 g-at yr^{-1}. The intrinsic isotopic fractionation factor was computed to be 1.007-1.015 in favor of $^{14}NO_3^-$. The total production of phosphate was estimated to be 3.1×10^7 - 4.7×10^7 g-at yr^{-1} of which at least 50% was produced from denitrification.

Nineteen water samples collected off Peru on the 1977 JOINT II cruise were analyzed for concentration and isotopic composition of the combined nitrate and nitrite. The average rate of denitrification in the oxygen-deficient zone was estimated to be 10 μM yr^{-1} using a one-dimensional steady-state model. The isotopic fraction-ation factor was determined to be 1.015.

Heavy nitrate produced in the denitrifying zone is redistributed by ocean circu-lation and mixing. Comparison of $\delta^{15}N$ values in different parts of the Pacific Ocean indicates that the dissolved nitrate in the intermediate water off southern California is 1-2 ‰ heavier than western and central Pacific Ocean values. This heavy nitrate could originate from the subsurface water mass off Baja California.

KINETICS AND MECHANISMS OF SEVERAL AMINO-ACID DIAGENETIC REACTIONS IN AQUEOUS SOLUTIONS AND IN FOSSILS

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The amino-acid racemization reaction has been used successfully in various geo-chronological and geothermometric applications. Additional diagenetic reactions have also found use in geological applications. The possible use of the decomposition reactions of two amino acids in the dating of foraminiferal tests from deep-sea cores and fossil bones and shells from terrestrial deposits has been investigated. A thorough discussion of the possible geochronological and geothermometric applications of these two chemical reactions is provided.

Preliminary results have shown that the decomposition of serine and threonine in foraminiferal tests in two Caribbean deep-sea cores (P6304-8 and -9) approximates irreversible first-order kinetics for at least the first 640,000 years. Similar investigations of bones from Murray Springs and Double Adobe in Arizona, and on Chione shells from four archaeological sites in coastal southern California provided evidence that the decomposition of serine and threonine in fossils from terrestrial deposits also approximate irreversible first-order kinetics for at least the first 10,000 years. The decomposition rate constants derived from these calibration samples can be used to estimate the age of other fossils that possess a similar temperature history. Preliminary tests on foraminifera from another Caribbean core (GS 7103-009-04) and from Deep Sea Drilling Project (DSDP) cores have shown encouraging results.

By mathematically coupling the decomposition reaction and racemization reaction, the age and the temperature history of a fossil sample can be determined without reference to other paleotemperature indicators or geochronological methods. This approach has been successfully applied to resolving the temperature history of Chione shells from the Del Mar Man site in southern California.

Also included in this thesis are the studies of the environmental effects on amino-acid racemization dating and the pH dependence of free amino-acid racemization rates.

pH and ground-water leaching, which were considered the two most important factors affecting the racemization dates, are shown to be much less important than temperature. From the results of this study on the pH dependence of free amino-acid racemization at 142°C, a revised method has been devised of calculating the half-lives of free amino-acid racemization at the pH and the temperature of natural waters. This new method demonstrates the necessity of obtaining a thorough understanding of the detailed mechanism of the chemical reaction under investigation. This understanding is essential for all the studies that involve the extrapolation of high-temperature kinetic data to the lower environmental temperatures.

BIOTRANSFORMATION AND BIOCONCENTRATION OF KEPONE BY MARINE BACTERIA, AND KEPONE-MICROBE INTERACTIONS

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Within the past ten years the James River and Chesapeake Bay have been contaminated with Kepone, a chlorinated insecticide which is chemically and physically stable. The migration of Kepone within the water column has extended in recent time to estuarine and marine waters where its interactions are unknown. Kepone has been found to induce toxic effects, e.g., scoliosis in fish, in higher marine organisms which inhabit coastal marine ecosystems. The purpose of the study described here was to determine the possible biotransformation and bioconcentration of Kepone by marine bacteria, the effects of Kepone on cellular physiology and the basis of Kepone resistance in marine microorganisms.

Alteration or biotransformation of Kepone was examined *in vitro* using marine sediment and water, and various bacterial strains. Initial studies with axenic and mixed bacterial isolates revealed that Kepone could not be utilized as a sole source of carbon and energy. However, significant growth was obtained if a supplemental carbon source was provided, suggesting that any biological alteration would have to take place via "cometabolism." Aerobic, pure and mixed cultures of marine bacteria were grown in minimal seawater salts broth amended with 100 µg/L Kepone and glucose, and incubated at 25°C for eight weeks in the dark. The culture supernatants of the appropriate controls and treatments were analyzed by electron-capture (^{63}Ni) gas-liquid chromatography (GLC) and high resolution electron-impact mass spectrometry (MS) to detect product formation. Both pure and mixed cultures yielded a monohydro or 9-chloro-Kepone product (1% of total added, MW=452) characterized by GLC with an R_f=0.84 relative to Kepone and mass spectrum ion clusters of 141, 182, 201, 235, 270, 319, and 417. A possible 8-chloro-Kepone product shown by GLC analysis could not be confirmed by MS since its total concentration was < 5 ng. Growth of a marine *Pseudomonas aeruginosa* anaerobically with nitrate as an alternate electron acceptor produced the same products. Studies utilizing marine sediments amended with Kepone revealed three additional products with retention times $\leq$ 0.5 of Kepone by GLC, which may represent conjugates of the parent molecule or additional dehalogenated

Kepone compounds.

Bioconcentration of Kepone by marine *P. aeruginosa* strain K03 was examined using various concentrations (10, 50 and 100 ng/mn) of ^{14}C-Kepone and different marine salts formulations. Accumulation of ^{14}C-Kepone was found to be a rapid, linear response dependent on the ^{14}C-Kepone concentration and suspension medium salts concentration. The maximum bioconcentration level of ca. 2.0×10^5 molecules/cell was reached in 15 and 30 minutes with the 50 and 100 ng Kepone/ml concentrations respectively, when a 20 mM marine salts medium was used. However, when a dilute, 2.0 mM salts buffer was used, accumulation of ^{14}C-Kepone occurred in less than one minute. These data indicate that the high degree of lipophilicity demonstrated by Kepone can result in extremely high biosorption partition coefficients, i.e., K_p = 4590 - 600,000, especially in marine waters where available organic matter, which binds Kepone, would be reduced.

The effects of various Kepone concentrations on the heterotrophic uptake and viability of marine microorganisms *in situ* was examined. Heterotrophic uptake of a mixture of ^{14}C-L-amino acids was determined by the Hobbie and Crawford technique and viable cells were determined by a modification of the procedure of Kogure, Simidu and Taga. Surface-water samples taken from the Chesapeake Bay were treated with Kepone concentrations ranging from 0.01 mg/L to 10 mg/L and incubated for 0.5 - 6 hours. In all of the water samples examined, the minimum inhibitory concentration affecting respiration and incorporation was 0.2 mg/L. Concentrations $\leq$ 0.01 mg Kepone/L caused little, usually 0-20%, inhibition of heterotrophic uptake and reduction in cell viability. Also, the percent reduction observed for water samples collected at various sample sites and times was similar in magnitude and rate. Pearson correlation analysis showed significant, α=0.05, correlation between heterotropic uptake at 0.5 hour and cell viability for all concentrations of Kepone and samples tested. It is concluded that concentrations of Kepone that are present in dissolved form in marine waters cause minimum effect on *in situ* heterotrophic uptake and cell viability.

Identification of 130 Kepone-resistant marine bacteria revealed only Gram negative bacteria, predominantly *Pseudomonas* spp. and *Vibrio* spp., which were further characterized by 36 biochemical, physiological and resistance tests. Numerical taxonomic

cluster analysis at the 70% similarity level showed that these Kepone-resistant strains possessed high degrees of pesticide, antibiotic, and heavy-metal resistance and the capability for oil degradation, nitrate reduction and oxidase and catalase activity. Oxygen-uptake studies and gel electrophoresis of cellular membrane proteins of various Kepone sensitive and resistant bacterial strains indicate that the effect of Kepone appears to center around the biosynthesis of cellular membrane constituents which may be necessary for cellular replication. Effects on cellular energy metabolism are secondary and very limited in degree with Gram negative bacteria, however Gram positive bacterial oxidative metabolism is severely affected.

STRUCTURE AND FUNCTION OF DEEP-SEA MICROBIAL POPULATIONS

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A major impetus behind the fundamental research in baromicrobiology is the growing need to understand biological processes as they occur under the hyperbaric conditions of the deep-ocean environment. Biogeochemical cycles in the marine environment have remained incompletely described due to a paucity of information on microbial metabolic rates of transformation of matter in the deep sea, though marine bacteria have been shown to be ubiquitous, even in the deepest regions of the world oceans.

Three populations: free-living organisms in the deep-ocean water column, bacteria in the sediment, and gut microflora of deep-sea benthic macrofauna have been distinguished by the respective endogenous utilization rates of natural populations at *in situ* pressure and temperature conditions. A Deep Ocean Sampler (DOS) has been developed which is capable of aseptically collecting 400 ml water samples from any depth and maintaining the *in situ* pressure and temperature on retrieval. In conjunction, a hyperbaric transfer system was developed for time-course analysis of activity of the samples. Subsamples of up to 100 ml are transferred to incubation chambers without decompression or exposure to sheer forces, or without dilution of the remaining sample in the DOS. The utilization rates of radio-labelled glutamate, acetate and amino-acid mixture, respiration to CO_2 and incorporation into the cellular fraction, have been determined by analysis of subsamples taken in the Puerto Rico Trench (3450-7730 m), the Atlantic Abyssal Plain (3550 m) and the Angolan and Cape Basins (5200 m). Average utilization rates ranged from 1.1×10^{-3} µg glutamate/liter/week in the Puerto Rico Trench to 1.0×10^{0} µg glutamate/liter/week in the northwest Atlantic. Utilization was found to be a function of the number of organisms in the samples (as direct microscopic counts), *in situ* pressure of incubation, and productivity of the benthic region. For example, samples of the relatively more productive Angolan Basin were observed to be significantly more active in glutamate conversion and mineralization than samples from the Cape Basin, of equivalent depth. Decompressed samples, run in parallel with the undecompressed samples, yielded

stimulated activity, 1.6 to <u>ca</u>. 10 fold greater than undecompressed samples. Metabolic activities of free-living populations of five deep-ocean water samples and three box cores, and gut flora of seven deep-sea benthic macrofauna collected from the Cape and Angolan Basins were directly comparable. Utilization rates (averages) observed were: water, 2.3×10^{-5} µg/ml/wk; sediment, 8.4 $\times 10^{-3}$ µg/g/wk; low activity gut microflora, 9.3×10^{-3} µg/g/wk; and active gut microflora, 2.8×10^{0} µg/g/wk. Samples of a deep-sea holuthurian and a benthic fish demonstrated very active gut microflora. The metabolic rates and growth of the repressurized suspensions were not inhibited or, in cases, accelerated by *in situ* pressure and temperature.

Metabolic activities of microbial populations can serve as indicators of rates of conversion and mineralization of organic matter in the deep ocean and, therefore, are of significance for understanding nutrient and energy cycles in the ocean. Estimates of endogenous rates of activity measured of microorganisms present in undecompressed deep-ocean water samples were determined using the Deep Ocean Sampler. Utilization rates, although very low, were found to vary according to environment and were stimulated by addition of substrate. Decompression, however, consistently resulted in stimulated activity, up to several fold. Indication of barophilic activity has been recorded for gut microflora, supporting the concept of adaptation to elevated pressures of the deep sea by microbial populations provided adequate nutrient levels.